Theoretical Studies of Electron Molecule Collision Processes

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Abstract

Theoretical studies of electron-atom and electron-molecule scattering are reported. Second Born scattering amplitudes for the scattering of electrons from helium have been calculated, with the matrix elements of the two particle Green's function being estimated using the closure approximation. Electron-molecular hydrogen amplitudes have also been calculated using a numerical quadrature scheme.

A multichannel method of applying Schwinger's variational theory, which utilises the closure approximation to estimate the second Born like terms required, is introduced and a discussion of possible future work in this area is given.

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I also have to thank my supervisor Dr. R. Maclagan.

The electron is not as simple as it looks.

-Sir William Lawerence Bragg

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Chapter 1

Introduction

This dissertation presents the results of the study undertaken by the author into the application of quantum scattering theory, to electron-atom and electron-molecule scattering. This chapter provides a comment on the original objectives and subsequent development of this work, and a short review of the proceeding chapters.

The original objective of this research program was to initiate studies into the theoretical determination of electron-molecule scattering data within the framework of non-relativistic quantum mechanics. This was the first attempt at studying this field within the theoretical chemistry group at the University of Canterbury, and so a large part of the initial work involved assimilating the relevant theory and studying the current theoretical methods. Once specific areas, within the field of theoretical scattering were identified as potential areas of research, work was undertaken in the development of numerical tools, required for the evaluation of the scattering data. Because of our lack of experience, emphasis was placed on the replication of published results to ensure our numerical techniques were correct. Unfortunately, only a limited amount of this work has been completed to date, leaving a section of study to be completed. This is discussed in chapter 8.

Chapters 2 and 3 of this thesis, give a brief introduction to the concepts of quantum scattering theory, discussed within the framework of spin-less scattering from a fixed center of force. The quantum mechanical system is treated using the Schrödinger formalism. The two Hamiltonians for the system are defined, and the various solutions of the resulting Schrödinger equation are introduced. Chapter 2 is based on the time dependent Schrödinger equation whereas chap-

ter 3 introduces the time independent formalism. Finally the theoretically derived scattering amplitude is related to the experimentally measurable differential cross section.

Chapter 4 deals with the specific extensions required to chapters 2 and 3 for electron-atom and electron-molecule scattering. Three areas relating to this are discussed. The fact that atoms and molecules can change their configuration means electronically inelastic processes are possible (rotationally and vibrationally inelastic processes are deferred to chapter 8). The target electrons are also free to deform their motions due to the presence of the incident electron. Also, the identical nature of the incident and target electrons must be treated correctly, as must the electron spin.

Two theoretical methods used in calculating scattering amplitudes are presented in chapter 5. Schwinger's variational principle, which has been successfully applied to low energy electron scattering, and Born's approximation, which has been extensively used to calculate high energy scattering data are introduced. Both the Schwinger variational principle and the second Born approximation require the evaluation of matrix elements of the multichannel Green's function. This in turn involves a summation over the infinite number of target eigenstates which must be approximated in some manner for practical calculation. One method of achieving this, known as the closure approximation, is discussed.

Chapters 6 and 7 outline the calculations performed on atomic helium and molecular hydrogen respectively. The initial work was directed at reproducing published results for the second Born scattering amplitudes from helium as a confirmation of our numerical methods. This being achieved, the treatment of scattering of electrons from H_2 was attempted, as an extension of these ideas. Also reported are the potential scattering results calculated using Schwinger's variational method.

Chapter 8 offers suggestions for future work, following on from the preliminary results obtained in chapters 6 and 7. It is argued that the closure approximation can be applied to the estimation of the second Born like matrix elements, required in the calculation of scattering amplitudes via the Schwinger variational principle. It is also suggested that for molecular scattering at intermediate energies, partial wave analysis may have advantages in terms of computational efficiency, when considering orientational averaging of the molecular frame adiabatic nuclei scattering amplitudes.

Chapter 9 provides a short set of conclusions.

Chapter 2

Introduction to the Theory of Scattering

This chapter gives a very short introduction to the basic concepts of scattering theory. The system considered is the scattering of a structureless, spin zero mass point from a fixed center of force. Although this is not a physically realizable system for atomic scattering, the concepts can be extended to real systems without difficulty. Treatment of the scattering event is via the Schrödinger equation rather than the Heisenberg or interaction frameworks [1]. The solutions of the Schrödinger equation, known as the scattering states, are introduced. The property which defines a scattering event, the fact that the scattering states become physically indistinguishable from asymptotic states satisfying a free particle Schrödinger equation, is discussed and finally the scattering operator is introduced. The scattering operator is fundamental to scattering theory and relates the asymptotic out state to the specified asymptotic in state.

2.1 Quantum Scattering Theory

The simplest scattering system to study theoretically is that of two structureless, spin-less particles which interact via a local, spatial function $V(\mathbf{r})$, called the *interaction potential.* The vector $\mathbf{r}$ is defined as the vector joining the center of mass of the two particles.

Experimental scattering typically involves one beam of particles impinging on a fixed target or two crossed beams of particles. The measured cross sections are thus defined relative to the

fixed laboratory coordinate frame. Theoretical studies of scattering systems are most naturally formulated in the center of mass coordinate system where the center of gravity of the whole system is fixed. It is always possible to separate the center of mass motion from the relative motions of the components of the system allowing transformation from the laboratory frame to the center of mass frame and back (see appendix A). Thus, any experimental measurements can be transformed to the corresponding center of mass coordinate system where comparison can be made to theoretical calculations.

If one particle is sufficiently heavier than the other, it can be expected that the fraction of the total momentum transferred to the heavy particle during the collision is negligible and thus to a good approximation the collision can be described in the center of mass coordinates of the heavy particle, neglecting the recoil of the heavy particle. This is equivalent to assuming that the heavy particle is of infinite mass with the light particle of mass m, being scattered from a fixed *center of force.*

2.2 The Schrödinger Picture

The time dependent Schrödinger equation for the system described above is

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle \tag{2.1}$$

where H is the full Hamiltonian for the system and $|\Psi(t)\rangle$ is the wave function describing the motion of the scattered particle. For the simple system considered here, the Hamiltonian can be written

$$H = -\frac{\mathbf{k}^2}{2m} + V \tag{2.2}$$

where the origin of the coordinate system is centered on the heavy particle. The $-\mathbf{k}^2/2m$ term represents the kinetic energy of the scattered particle and the interaction potential, $V(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}')\langle\mathbf{r}|V|\mathbf{r}'\rangle$ is defined relative to the center of mass of the heavy, target particle.

2.2.1 The Scattering States

The state which satisfies eqn 2.1 and in the infinite past ($t \rightarrow -\infty$), describes a freely moving wave packet with a momentum distribution centered about the vector $\mathbf{k_1}$, is written $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$. A definition of the free wave packet, $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle = |\Psi_{\mathbf{k_1}}(t)\rangle\,(t \ll 0)$ can be found in most elementary quantum mechanics texts [2]. From the states $|\Phi_{\mathbf{k}}(t)\rangle$ satisfying the free particle Schrödinger equation

$$i\frac{\partial}{\partial t}|\Phi_{\mathbf{k}}(t)\rangle = -\frac{\mathbf{k}^2}{2m}|\Phi_{\mathbf{k}}(t)\rangle \tag{2.3}$$

the wave packet is given by

$$|\Psi_{\mathbf{k_1}}(t)\rangle = \int \psi_{\mathbf{k_1}}(\mathbf{k})|\Phi_{\mathbf{k}}(t)\rangle d\mathbf{k} \tag{2.4}$$

where $\psi_{\mathbf{k_1}}(\mathbf{k}) = \langle\Phi_{\mathbf{k}}(t)|\Psi_{\mathbf{k_1}}(t)\rangle$ the subscript $\mathbf{k_1}$ referring to the fact that $\psi_{\mathbf{k_1}}(\mathbf{k})$ is peaked about the vector $\mathbf{k_1}$.

The state $|\Psi_{\mathbf{k_1}}(t)\rangle$ cannot be monochromatic ($|\Psi_{\mathbf{k_1}}(t)\rangle = |\Phi_{\mathbf{k_1}}(t)\rangle$) because then it would not be a normalizable function. Nevertheless, the momentum distribution is sharply peaked about the incident momentum vector $\mathbf{k_1}$.

Generally, the basis used to expand freely evolving wave packets, is the set of improper free wave states

$$\langle\mathbf{r}|\Phi_{\mathbf{k}}(t)\rangle = e^{i(\mathbf{k}\cdot\mathbf{r}-E_k t)}. \tag{2.5}$$

A second basis, which is utilised in the theory of scattering is the *Angular Momentum* basis. These functions satisfy the homogeneous Schrödinger equation, eqn 2.3 written in spherical polar coordinates. The spatial representation of these functions, for the specific angular momentum given by the quantum numbers L and M, can be written,

$$\langle\mathbf{r}|\Phi^{\mathrm{AM}}_{\mathbf{k},LM}(t)\rangle = h^{(1)}_L(kr)Y^*_{LM}(\hat{\mathbf{r}})Y_{LM}(\hat{\mathbf{k}})e^{-iE_k t} \tag{2.6}$$

where $h^{(1)}_L(kr)$ is the Lth order Hankel function and Y_{LM} are spherical harmonic functions.

2.2.2 The Spatial Description of a Scattering Event

Considering the time evolution of the spatial component of the state $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$, at times $t \ll 0$ the motion of the incident particle is described by a freely moving wave packet. For reasons discussed in chapter 3, the wave packet is highly peaked in the momentum component, about the incident momentum $\mathbf{k_1}$. As time runs, the particle eventually comes under the influence of the interaction potential $V(\mathbf{r})$, and so the motion deviates from the free motion in response to the $V(\mathbf{r})$. The wave packet spreads due to the interaction, until a time such that the wave packet has moved sufficiently far from the scattering center that the interaction potential no longer has any influence, and the state $\langle \mathbf{r}|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ again evolves as a free state. In contrast to the times $t \to -\infty$ where $\langle \mathbf{r}|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ is a collimated wave packet of momentum about $\mathbf{k_1}$ expanded in free wave functions, the state as $t \to \infty$ is expanded in angular momentum states. Thus $\langle \mathbf{r}|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ as $t \to \infty$ is described by a set of spreading spherical waves modulated by an angular factor which depends on the specific form of the interaction potential. Fig 2-1 attempts to give a basic pictorial representation of the time evolution of the $\langle \mathbf{r}|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ state.

The above description of the time evolution of the state $\langle \mathbf{r}|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ from $-\infty \to t \to \infty$ can be inverted so that initially the state of the system is described as a set of incoming spherical waves which impinge on the target and produce a collimated, nearly monochromatic outgoing wave packet with outgoing momenta $-\mathbf{k_1}$ (see fig 2-2). This is perhaps a less physically meaningful process but it is nonetheless theoretically justified. This idea can be extended such that the state $\langle \mathbf{r}|\Psi^{(-)}_{\mathbf{k_2}}(t)\rangle$ is defined as the state which at time, $t \to -\infty$ is given by a freely evolving incoming spherical wave packet which 'scatters' off the target and produces a collimated wave packet, peaked about the outgoing momenta $\mathbf{k_2}$.

The time evolution of the states $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ and $|\Psi^{(-)}_{\mathbf{k_2}}(t)\rangle$ can be written

$t=-\infty$		t		$t=\infty$
$\lvert\Psi_{\mathbf{k_1},(in)}\rangle$	$\to$	$\lvert\Psi^{(+)}_{\mathbf{k_1}}\rangle$	$\to$	$\lvert\bar{\Psi}_{(out)}\rangle$
$\lvert\bar{\Psi}_{(in)}\rangle$	$\to$	$\lvert\Psi^{(-)}_{\mathbf{k_2}}\rangle$	$\to$	$\lvert\Psi_{\mathbf{k_2},(out)}\rangle$

The states $|\Psi_{(in/out)}\rangle$ are well defined asymptotes of the states $|\Psi^{(\pm)}\rangle$. They describe the motion of a free particle with momentum $\mathbf{k_1}/\mathbf{k_2}$ and are written in terms of the free wave

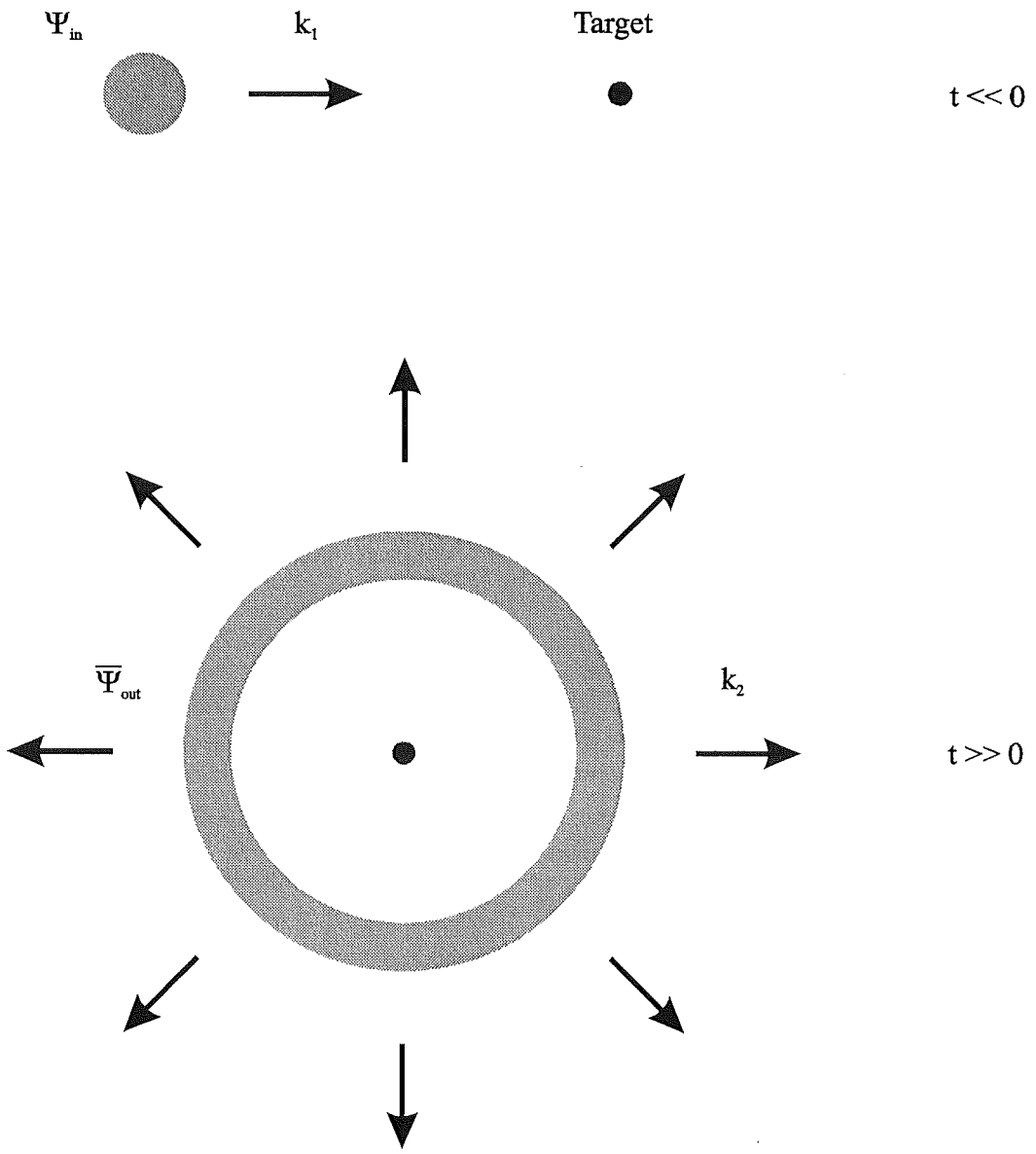


Figure 2-1: Pictorial representation of a scattering event with outgoing spherical wave boundary conditions

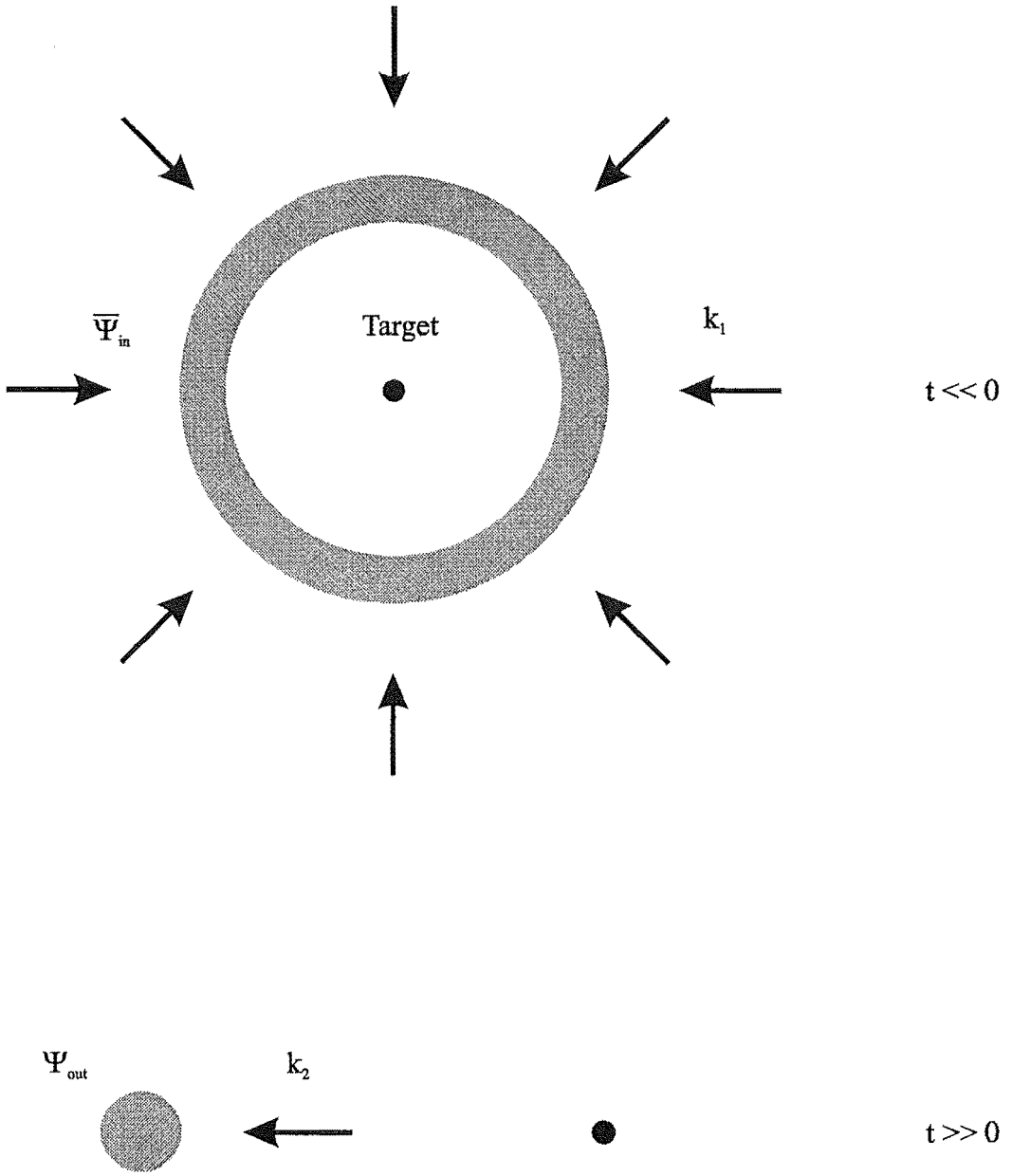


Figure 2-2: Pictorial representation of a scattering event with incoming spherical wave boundary conditions

functions of eqn 2.5. The states $|\bar{\Psi}_{(in/out)}\rangle$ are spherical wave states expanded in the basis of angular momentum functions of eqn 2.6 which are controlled in the sense that their form is determined by the particular asymptote $|\Psi_{(in/out)}\rangle$ and the interaction potential.

Typically in experimental scattering studies, the incident particles are prepared as a mono-energetic beam or pulse which is directed at a target and the angular distribution of the scattered particles measured. All atomic scale scattering experiments prepare and measure the particles in free states where the interaction with the target has dropped to zero. So, a theoretical quantity which forms the basis of comparison between theory and experiment is the probability of finding the system at $t = \infty$ as a freely moving wave packet with momenta $\mathbf{k_2}$ given that the state at $t = -\infty$ was a freely moving wave packet with momenta $\mathbf{k_1}$. This probability is simply the square of the overlap matrix between the states $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ and $|\Psi^{(-)}_{\mathbf{k_2}}(t)\rangle$ evaluated at some arbitrary time taken as $t = 0$,

$$p(\mathbf{k_2};\mathbf{k_1}) = |\langle\Psi^{(-)}_{\mathbf{k_2}}(0)|\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle|^2. \tag{2.7}$$

Evidently the overlap matrix

$$s(\mathbf{k_2};\mathbf{k_1}) = \langle\Psi^{(-)}_{\mathbf{k_2}}(0)|\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle \tag{2.8}$$

gives the probability amplitude that the system will make the transition from the state $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ to the state $|\Psi^{(-)}_{\mathbf{k_2}}(t)\rangle$ at $t = 0$.

2.2.3 The Asymptotic States

As mentioned previously, the state $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ as t becomes large and negative, evolves as a free state, unaffected by the interaction potential which is assumed to be of finite range. Thus as $t \to -\infty$ the state $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ will become indistinguishable from the state $|\Psi_{\mathbf{k_1},(in)}(t)\rangle$ satisfying the Schrödinger equation

$$i\frac{\partial}{\partial t}|\Psi_{\mathbf{k_1},(in)}(t)\rangle = H_0|\Psi_{\mathbf{k_1},(in)}(t)\rangle \tag{2.9}$$

where the Hamiltonian H_0 is $H_0 = H - V$. Now

$$|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle \rightarrow |\Psi_{\mathbf{k_1},(in)}(t)\rangle \quad \text{as} \quad t \rightarrow -\infty. \tag{2.10}$$

Because of the time independence of the Hamiltonians H and H_0, eqns 2.1 and 2.9 can be solved symbolically as

$$|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle = e^{-iHt}|\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle \tag{2.11}$$

$$|\Psi_{\mathbf{k_1},(in)}(t)\rangle = e^{-iH_0t}|\Psi_{\mathbf{k_1},(in)}(0)\rangle. \tag{2.12}$$

The operators $e^{-iH(t-t')}$ and $e^{-iH_0(t-t')}$ are referred to as time evolution operators as they relate the state of the system at the time t to the system at the time t'. The expression 2.10 can now be written as

$$\lim_{t\rightarrow-\infty}\left(e^{-iHt}|\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle - e^{-iH_0t}|\Psi_{\mathbf{k_1},(in)}(0)\rangle\right) = 0 \tag{2.13}$$

or

$$\lim_{t\rightarrow-\infty}\left(e^{-iHt}|\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle = e^{-iH_0t}|\Psi_{\mathbf{k_1},(in)}(0)\rangle\right). \tag{2.14}$$

Thus

$$\begin{aligned} |\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle &= \lim_{t\rightarrow-\infty} e^{iHt}e^{-iH_0t}|\Psi_{\mathbf{k_1},(in)}(0)\rangle \\ &= \Omega^{(+)}|\Psi_{\mathbf{k_1},(in)}(0)\rangle. \end{aligned} \tag{2.15}$$

The operator $\Omega^{(+)}$ is one of two *Møller* operators. The other, $\Omega^{(-)}$, is defined as

$$\Omega^{(-)} = \lim_{t\rightarrow\infty} e^{iHt}e^{-iH_0t} \tag{2.16}$$

and is applied in the same way as eqn 2.15 to give the actual scattering state at $t = 0$ in terms of the out asymptote

$$|\Psi^{(-)}_{\mathbf{k_2}}(0)\rangle = \Omega^{(-)}|\Psi_{\mathbf{k_2},(out)}(0)\rangle. \tag{2.17}$$

$|\Psi_{\mathbf{k_2},(out)}(t)\rangle$ as with $|\Psi_{\mathbf{k_1},(in)}(t)\rangle$ is a solution of eqn 2.9 .

The operators $\Omega^{(+)}$ and $\Omega^{(-)}$ are *isometric*[1] and thus preserve the norm of the vectors they operate on. Further

$$\Omega^{(+)\dagger}\Omega^{(+)} = \Omega^{(-)\dagger}\Omega^{(-)} = \mathbf{1}. \tag{2.18}$$

but $\Omega^{(+)}\Omega^{(+)\dagger} \neq \mathbf{1}$ and similarly with $\Omega^{(-)}$.

If the actual scattering orbit of the particle is $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ then

$$\begin{aligned} |\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle &= \Omega^{(+)}|\Psi_{\mathbf{k_1},(in)}(0)\rangle \\ &= \Omega^{(-)}|\bar{\Psi}_{(out)}(0)\rangle. \end{aligned} \tag{2.19}$$

Now operating on the left of eqn 2.19 by $\Omega^{(-)\dagger}$ gives

$$|\bar{\Psi}_{(out)}(0)\rangle = S|\Psi_{\mathbf{k_1},(in)}(0)\rangle \tag{2.20}$$

where the Scattering Operator S is

$$S = \Omega^{(-)\dagger}\Omega^{(+)}. \tag{2.21}$$

The scattering operator gives the asymptotic state $|\bar{\Psi}_{(out)}(0)\rangle$ directly in terms of the *in* asymptote and is thus a fundamental expression in scattering theory.

Expression 2.20 can be inverted to give the controlled *in* asymptote in terms of the *out* asymptote $|\Psi_{\mathbf{k_2},(out)}\rangle$,

[1] An isometric operator of the Hilbert space $\mathcal{H}$ is a linear operator, which is defined on the whole of $\mathcal{H}$, and preserves the norm. The difference between isometric operators and *unitary operators* is that the range of a unitary operator is equal to the domain over which it is defined. The range of an isometric operator, defined on $\mathcal{H}$ is not necessarily the whole Hilbert space $\mathcal{H}$.

$$|\bar{\Psi}_{(in)}(0)\rangle = S^{\dagger}|\Psi_{\mathbf{k_2},(out)}(0)\rangle. \tag{2.22}$$

The operator S is a *unitary* operator, which means it preserves the norm which is required to conserve energy. It also maps the range of scattering states onto itself, again as required due to the orthogonality of the scattering and bound states and the fact that the combination of scattering and bound states constitutes the whole range of possible one particle states of the system.

2.3 The Green's Functions and the Lippmann-Schwinger Equation

The time independent and time dependent Green's functions are introduced in appendix B along with some of their properties and uses in perturbation and scattering theories.

The time dependent Schrödinger equation for the scattering system is (see eqn 2.1)

$$\begin{aligned} i\frac{\partial}{\partial t}|\Psi^{(\pm)}(t)\rangle &= H|\Psi^{(\pm)}(t)\rangle \\ \left(i\frac{\partial}{\partial t} - H_0\right)|\Psi^{(\pm)}(t)\rangle &= V|\Psi^{(\pm)}(t)\rangle \end{aligned} \tag{2.23}$$

and the associated homogeneous equations are (see eqn 2.9)

$$\begin{aligned} i\frac{\partial}{\partial t}|\Psi_{in/out}(t)\rangle &= H_0|\Psi_{in/out}(t)\rangle \\ \left(i\frac{\partial}{\partial t} - H_0\right)|\Psi_{in/out}(t)\rangle &= 0. \end{aligned} \tag{2.24}$$

These two equations are in precisely the form of equations B.36 and B.35 with

$$\begin{aligned} L &= H_0 \\ c &= 1 \end{aligned}$$

$$
\begin{aligned}
f(t) &= V|\Psi^{(\pm)}(t)\rangle \\
|\phi(t)\rangle &= |\Psi_{in/out}(t)\rangle \\
|\psi(t)\rangle &= |\Psi^{(\pm)}(t)\rangle.
\end{aligned}
$$

Thus, the solutions of eqn 2.23 are given by eqn B.37,

$$|\Psi^{(+)}(t)\rangle = |\Psi_{in}(t)\rangle + \int dt' g^{+}(t,t')V|\Psi^{(+)}(t)\rangle \tag{2.25}$$

and

$$|\Psi^{(-)}(t)\rangle = |\Psi_{out}(t)\rangle + \int dt' g^{-}(t,t')V|\Psi^{(-)}(t)\rangle. \tag{2.26}$$

The equations 2.25 and 2.26 are referred to as the *Lippmann-Schwinger* equations, and are integral equations for the scattering states $|\Psi^{(\pm)}(t)\rangle$. For eqn 2.25 the integral over t' should run from $-\infty \rightarrow t$ but the Green's function $g^{+}(t,t') = 0$ for $t' > t$ so the limits can be taken as $-\infty$ and ∞. A similar argument holds for eqn 2.26.

The functions $|\Psi^{(\pm)}(t)\rangle$ can be shown to be orthogonal.

$$\langle \Psi^{(+)}_{\mathbf{k_1}}(t)|\Psi^{(+)}_{\mathbf{k_2}}(t)\rangle = \delta(\mathbf{k_1} - \mathbf{k_2}), \tag{2.27}$$

and similarly for $|\Psi^{(-)}(t)\rangle$. This is a general expression of the orthogonality theorem of section 2.3.1, and combined with a general completeness theorem can be stated simply as

$$\langle \Psi^{(\pm)}_{\nu}|\Psi^{(\pm)}_{\mu}\rangle = \delta_{\nu\mu} \tag{2.28}$$

where the function $|\Psi^{(+)}_{\nu}\rangle$ is an eigenfunction of 2.1, which must be a member of the set of solutions of eqn 2.25 combined with the bound states of the Hamiltonian H, and so $|\Psi^{(+)}_{\nu}\rangle \in \{\Psi_b(t), \Psi^{(+)}_{\mathbf{k_1}}(t)\}$. Similarly with $|\Psi^{(-)}_{\nu}\rangle$.

2.3.1 Further Remarks

The above argument rests on a number of assumptions and mathematical theorems not explicitly mentioned, some of which will be introduced here.

The Asymptotic Condition, Orthogonality and Asymptotic Completeness

The asymptotic condition states that for every asymptote $|\Psi_{in/out}(t)\rangle$ there is a corresponding scattering state $|\Psi^{(\pm)}(t)\rangle$. That is, for every vector $|\Psi_{in/out}(0)\rangle$ in the Hilbert space of the system $\mathcal{H}$ there is a solution of the Schrödinger equation $|\Psi^{(\pm)}(t)\rangle = e^{-iHt}|\Psi^{(\pm)}(0)\rangle$, which is equivalent to the free orbit $e^{-iH_0t}|\Psi_{in/out}(0)\rangle$ as $t \to \mp\infty$, This requires

$$\lim_{t\to\mp\infty}\left(e^{-iHt}|\Psi^{(\pm)}(0)\rangle - e^{-iH_0t}|\Psi_{in/out}(0)\rangle\right) = 0 \tag{2.29}$$

or

$$\lim_{t\to\mp\infty}\left(|\Psi^{(\pm)}(0)\rangle - e^{iHt}e^{-iH_0t}|\Psi_{in/out}(0)\rangle\right) = 0, \tag{2.30}$$

for all $|\Psi_{in/out}\rangle$ in $\mathcal{H}$.

Taylor [3] shows that this is true for a Gaussian function and thus concludes, since any vector in $\mathcal{H}$ can be arbitrarily well approximated as a linear combination of Gaussians, this also follows for all $|\Psi_{in/out}\rangle$ in $\mathcal{H}$.

Given the system defined by the Hamiltonian in eqn 2.2, all the possible one particle states satisfying eqn 2.1 are given by $\{\Psi(t)\}$. For an interaction potential satisfying the conditions,

1.

$$\lim_{r\to\infty} V(\mathbf{r}) = O(r^{-3-\epsilon}) \tag{2.31}$$

2.

$$\lim_{r\to 0} V(\mathbf{r}) = O(r^{-3/2+\epsilon}) \tag{2.32}$$

3. $V(\mathbf{r})$ is continuous over all $\mathbf{r}$, except possibly at a finite number of finite discontinuities.

the Hilbert space of all possible states of H, written $\mathcal{H}$, can be broken into the subspace spanned by any possible bound states supported by the interaction potential, written $\mathcal{B}$, the orthogonal compliment of which is the space spanned by the scattering states of the system

$\mathcal{S}$. Thus, all the possible bound states of the system $\{\Psi_b(t)\}$ are orthogonal to the scattering states $\{\Psi_s(t)\}$, and the sum of the two constitutes all the possible states of the system.

The orthogonality of $\mathcal{B}$ and $\mathcal{S}$ can be seen in a non-rigorous way by considering the overlap between the bound state $|\Psi_b(t)\rangle$ in $\mathcal{B}$ and the scattering state $|\Psi^{(+)}_{\mathbf{k_1}}(t)\rangle$ in $\mathcal{S}$. At $t = 0$,

$$\langle\Psi_b(0)|\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle. \tag{2.33}$$

Now, the overlap of these two states as $t \to -\infty$ is given by

$$\begin{aligned}\lim_{t\to-\infty}\langle e^{-iHt}\Psi_b(0)|e^{-iHt}\Psi^{(+)}_{\mathbf{k_1}}(0)\rangle = \\ \lim_{t\to-\infty}\langle e^{-iHt}\Psi_b(0)|e^{-iH_0t}\Psi_{\mathbf{k_1},(in)}(0)\rangle.\end{aligned} \tag{2.34}$$

Considering the spatial components of the two states then the action of the time evolution operator e^{-iHt} on the bound state $\langle\mathbf{r}|e^{iHt}|\Psi_b(0)\rangle$ leaves it localised about the interaction potential, $V(\mathbf{r})$. The operation $\langle\mathbf{r}|e^{-iH_0t}|\Psi_{\mathbf{k_1},(in)}(0)\rangle$ on the other hand, produces a wave packet centered at $r = \infty$ and thus the overlap matrix 2.34 is zero and because it is time independent, must be zero at all times implying the spaces $\mathcal{B}$ and $\mathcal{S}$ are orthogonal.

Taking the space $\mathcal{S}_+$ to be the space spanned by all the scattering states $|\Psi^{(+)}(t)\rangle$ and similarly $\mathcal{S}_-$ as the space spanned by $|\Psi^{(-)}(t)\rangle$ then for a scattering theory to asymptotically complete, the spaces $\mathcal{S}_+$ and $\mathcal{S}_-$ must be equal, $\mathcal{S}_+ = \mathcal{S}_- = \mathcal{S}$ and $\mathcal{S} + \mathcal{B} = \mathcal{H}$. Because the bound and scattering states are orthogonal, this is equivalent to saying $\mathcal{S}_+ = \mathcal{S}_- = \mathcal{S}$ and the space $\mathcal{S}$ is the space spanned by all vectors in $\mathcal{H}$ which are orthogonal to the bound states. Potentials satisfying the conditions 1, 2 and 3, can be shown to be asymptotically complete.

Vector and Operator Convergence

The vector $\psi(t)$ in $\mathcal{H}$, is said converge to zero strongly as $t \to \infty$, if

$$\lim_{t\to\infty}|\psi(t)| \to 0. \tag{2.35}$$

For any normalized vector ϕ in $\mathcal{H}$,

$$\begin{aligned}\lim_{t\to\infty}|\langle\phi|\psi(t)\rangle| &\leq \lim_{t\to\infty}|\phi|\cdot|\psi(t)| \\ &= \lim_{t\to\infty}|\psi(t)| \\ &\to 0. \end{aligned} \tag{2.36}$$

In words, this says that if the vector $\psi(t)$ in $\mathcal{H}$ converges strongly to zero as $t \to \infty$, all the components of $\psi(t)$ measured in any normalized basis spanning $\mathcal{H}$ also converge to zero. The converse is not necessarily true, and if it is not the case that $|\psi(t)| \to 0$ even though all it's components in the basis $\{\phi\}$ spanning $\mathcal{H}$ tend to zero, the vector $\psi(t)$ is said to converge weakly to zero as $t \to \infty$.

The vector $\psi(t)$ can now be said to converge strongly to the vector ψ in the limit $t \to \infty$ if

$$\lim_{t\to\infty}|\psi(t) - \psi| = 0 \tag{2.37}$$

and the other convergence results follow.

Given that any physically measurable state can be expanded in an orthonormal basis spanning $\mathcal{H}$, the statement that all the components of the vector $\psi(t)$ in the basis $\{\phi\}$ converge to the components of ψ in the limit $t \to \infty$ means the state $\psi(t)$ is physically indistinguishable from ψ in the limit $t \to \infty$. This is the requirement we have for the scattering states $\Psi^{(\pm)}$ with respect to the asymptotic states $\Psi_{in/out}$ and thus it is guaranteed that $\Psi^{(\pm)}$ will be physically indistinguishable form $\Psi_{in/out}$ if $\Psi^{(\pm)}$ converges strongly to $\Psi_{in/out}$ in the limit $t \to \infty$.

Operator convergence can be considered in terms of vector convergence. An operator A is said to have a limit as $t \to \infty$ if for every vector $|\psi(t)\rangle$

$$\lim_{t\to\infty}(A|\psi(t)\rangle - |\phi\rangle) = 0. \tag{2.38}$$

That is, the vector defined as $A|\psi(t)\rangle$ converges to the vector $|\phi\rangle$ as described above.

Chapter 3

Time Independent Scattering and the Differential Cross Section

In this chapter, the theoretically derived scattering operator from chapter 2, is related to the experimentally measurable, differential cross section. The two approaches are linked via time independent scattering theory and the *scattering matrix*. The time independent solutions of the Schrödinger equation are discussed and the scattering matrix introduced. The scattering matrix is decomposed into two components and finally the differential cross section is derived in terms of the *scattering amplitude*, which is a theoretical quantity present in the reduced scattering matrix.

3.1 The Stationary Scattering States

Equation 2.9 can be written

$$i\frac{\partial}{\partial t}|\Phi(t)\rangle = -\frac{\mathrm{k}^2}{2m}|\Phi(t)\rangle. \tag{3.1}$$

which has a set of standard solutions

$$|\Phi_{\mathrm{k}}(t)\rangle = |\phi_{\mathrm{k}}\rangle e^{-iE_k t} \tag{3.2}$$

where $E_k = k^2/2m$ and the spatial representation of $|\phi_{\mathrm{k}}\rangle$ is the familiar plane wave

$$\langle \mathbf{r}|\phi_{\mathbf{k}}\rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{3.3}$$

Now the eqn 3.2 as it stands, cannot be a solution of eqn 2.9 because of the additional requirement that $\Psi_{in/out}$ must be normalizable. Obviously the asymptotes $|\Psi_{in/out}\rangle$, are generated by the superposition of the functions $|\phi_{\mathbf{k}}\rangle$,

$$\begin{aligned} |\Psi_{(in/out)}(t)\rangle &= \int |\phi_{\mathbf{k}}\rangle\langle\phi_{\mathbf{k}}|\Psi_{(in/out)}(t)\rangle e^{iE_k t} d\mathbf{k} \\ &= \int |\phi_{\mathbf{k}}\rangle \psi(\mathbf{k}) e^{iE_k t} d\mathbf{k} \end{aligned} \tag{3.4}$$

This is what is meant by the wave packet. Now from eqn 2.15

$$\begin{aligned} |\Psi^{(+)}_{\mathbf{k}_1}(0)\rangle &= \Omega^{(+)}|\Psi_{\mathbf{k}_1,(in)}(0)\rangle \\ &= \Omega^{(+)} \int |\phi_{\mathbf{k}}\rangle \psi_{\mathbf{k}_1}(\mathbf{k}) d\mathbf{k} \\ &= \int \Omega^{(+)}|\phi_{\mathbf{k}}\rangle \psi_{\mathbf{k}_1}(\mathbf{k}) d\mathbf{k} = \int |\phi^{(+)}_{\mathbf{k}}\rangle \psi_{\mathbf{k}_1}(\mathbf{k}) d\mathbf{k} \end{aligned} \tag{3.5}$$

The subscript $\mathbf{k}_1$ notes the fact that the function $\psi_{\mathbf{k}_1}(\mathbf{k})$ is peaked about the momenta $\mathbf{k}_1$. The states $|\phi^{(+)}_{\mathbf{k}}\rangle = \Omega^{(+)}|\phi_{\mathbf{k}}\rangle$ are time independent and are referred to as the *stationary scattering states.*

The set of states $\{\phi^{(-)}_{\mathbf{k}}\}$ are similarly defined as $|\phi^{(-)}_{\mathbf{k}}\rangle = \Omega^{(-)}|\phi_{\mathbf{k}}\rangle$. The functions $|\phi^{(\pm)}_{\mathbf{k}}\rangle$ are eigenfunctions of the Hamiltonian H.

$$\begin{aligned} H|\phi^{(\pm)}_{\mathbf{k}}\rangle &= H\Omega^{(\pm)}|\phi_{\mathbf{k}}\rangle \\ &= \Omega^{(\pm)} H_0 |\phi_{\mathbf{k}}\rangle \\ &= E_k \Omega^{(\pm)}|\phi_{\mathbf{k}}\rangle = E_k |\phi^{(\pm)}_{\mathbf{k}}\rangle \end{aligned} \tag{3.6}$$

$E_k = k^2/2m$. This expression uses the so called *intertwining relation* $H\Omega^{(\pm)} = \Omega^{(\pm)} H_0$.

3.1.1 Time Independent Lippmann-Schwinger Equations

The function $|\phi_{\mathbf{k}}\rangle$ is an eigenfunction of the Hamiltonian H_0, with eigenvalue $E_k = k^2/2m$. Writing this along with the result of eqn 3.6 as,

$$(E_k - H_0)\,|\phi_{\mathbf{k}}\rangle = 0 \tag{3.7}$$

$$(E_k - H_0)\,|\phi_{\mathbf{k}}^{(\pm)}\rangle = V|\phi_{\mathbf{k}}^{(\pm)}\rangle \tag{3.8}$$

and using the results of section B.1,

$$|\phi_{\mathbf{k}}^{(\pm)}\rangle = |\phi_{\mathbf{k}}\rangle + G_0^{\pm}(E_k)V|\phi_{\mathbf{k}}^{(\pm)}\rangle \tag{3.9}$$

which is the analogue of eqns 2.25 and 2.26 for the time dependent case.

The orthogonality of the states $|\phi_{\mathbf{k}}^{(\pm)}\rangle$ can be shown by

$$\begin{aligned}\langle\phi_{\mathbf{k_1}}^{(+)}|\phi_{\mathbf{k_2}}^{(+)}\rangle &= \langle\Omega^{(+)}\phi_{\mathbf{k_1}}|\Omega^{(+)}\phi_{\mathbf{k_2}}\rangle \\ &= \langle\phi_{\mathbf{k_1}}|\Omega^{(+)\dagger}\Omega^{(+)}\phi_{\mathbf{k_2}}\rangle \\ &= \langle\phi_{\mathbf{k_1}}|\phi_{\mathbf{k_2}}\rangle = \delta(\mathbf{k_1} - \mathbf{k_2}).\end{aligned} \tag{3.10}$$

This fact is used to show the orthogonality of the states $|\Psi_{\mathbf{k}}^{(\pm)}\rangle$ from section 2.3.

Now from eqn 3.9 and using eqns B.59 and B.53

$$|\phi_{\mathbf{k}}^{(\pm)}\rangle = \left(1 + G^{\pm}(E_k)V\right)|\phi_{\mathbf{k}}\rangle. \tag{3.11}$$

This equation gives $|\phi_{\mathbf{k}}^{(\pm)}\rangle$ directly in terms of the plane wave states $|\phi_{\mathbf{k}}\rangle$ but at the expense of introducing the full Green's function $G^{\pm}$.

Substituting the complete set of states $\{\phi_{\mathbf{k}'}\}$ into eqn 2.20 gives

$$|\bar{\Psi}_{(out)}(0)\rangle = S|\Psi_{\mathbf{k_1},(in)}(0)\rangle$$

$$
\begin{aligned}
&= \int S|\phi_{\mathbf{k}'}\rangle\langle\phi_{\mathbf{k}'}|\Psi_{\mathbf{k}_1,(in)}(0)\rangle d\mathbf{k}' \\
&= \int S|\phi_{\mathbf{k}'}\rangle\psi_{\mathbf{k}_1}(\mathbf{k}')d\mathbf{k}', \qquad (3.12)
\end{aligned}
$$

and so

$$
\langle\phi_{\mathbf{k}''}|\bar{\Psi}_{(out)}\rangle = \int\langle\phi_{\mathbf{k}''}|S|\phi_{\mathbf{k}'}\rangle\psi_{\mathbf{k}_1}(\mathbf{k}')d\mathbf{k}'. \qquad (3.13)
$$

The term

$$
S_{\mathbf{k}'',\mathbf{k}'} = \langle\phi_{\mathbf{k}''}|S|\phi_{\mathbf{k}'}\rangle. \qquad (3.14)
$$

is called the *scattering matrix*, $S_{\mathbf{k}'',\mathbf{k}'}$, being the matrix elements of the scattering operator (eqn 2.21) in the basis of plane wave states.

The right hand side of eqn 3.13 gives the probability amplitude, that the state $|\bar{\Psi}_{(out)}\rangle$ contains the momentum component $\mathbf{k}''$.

3.2 The Decomposition of the Scattering Matrix

From the definition of the scattering operator

$$
\begin{aligned}
S_{\mathbf{k}'',\mathbf{k}'} &= \langle\phi_{\mathbf{k}''}|S|\phi_{\mathbf{k}'}\rangle \\
&= \langle\phi^{(-)}_{\mathbf{k}''}|\phi^{(+)}_{\mathbf{k}'}\rangle \\
&= \langle\phi^{(-)}_{\mathbf{k}''} - \phi^{(+)}_{\mathbf{k}''}|\phi^{(+)}_{\mathbf{k}'}\rangle + \langle\phi^{(+)}_{\mathbf{k}''}|\phi^{(+)}_{\mathbf{k}'}\rangle. \qquad (3.15)
\end{aligned}
$$

The second term in eqn 3.15, $\langle\phi^{(+)}_{\mathbf{k}''}|\phi^{(+)}_{\mathbf{k}'}\rangle$ is simply the momentum delta function $\delta(\mathbf{k}''-\mathbf{k}')$. The first term is

$$
\langle\phi^{(-)}_{\mathbf{k}''} - \phi^{(+)}_{\mathbf{k}''}|\phi^{(+)}_{\mathbf{k}'}\rangle = \langle\left(\left(G^-(E_{k''}) - G^+(E_{k''})\right)V\phi_{\mathbf{k}''}|\phi^{(+)}_{\mathbf{k}'}\right\rangle \qquad (3.16)
$$

from eqn 3.11. Using eqn B.5 this becomes

$$
\begin{aligned}
&\langle \phi^{(-)}_{\mathbf{k}''} - \phi^{(+)}_{\mathbf{k}''} | \phi^{(+)}_{\mathbf{k}'} \rangle \\
&= \lim_{\eta \to 0^+} \langle \phi_{\mathbf{k}''} | V \left((E_{k''} - H - i\eta)^{-1} - (E_{k''} - H + i\eta)^{-1} \right) | \phi^{(+)}_{\mathbf{k}'} \rangle \\
&= \lim_{\eta \to 0^+} \langle \phi_{\mathbf{k}''} | V \left((E_{k''} - E_{k'} - i\eta)^{-1} - (E_{k''} - E_{k'} + i\eta)^{-1} \right) | \phi^{(+)}_{\mathbf{k}'} \rangle \\
&= \lim_{\eta \to 0^+} \frac{-2i\eta}{(E_{k''} - E_{k'})^2 + \eta^2} \langle \phi_{\mathbf{k}''} | V | \phi^{(+)}_{\mathbf{k}'} \rangle \\
&= -2\pi i \delta(E_{k''} - E_{k'}) \langle \phi_{\mathbf{k}''} | V | \phi^{(+)}_{\mathbf{k}'} \rangle \qquad (3.17)
\end{aligned}
$$

so finally

$$
S_{\mathbf{k}'',\mathbf{k}'} = \delta(\mathbf{k}'' - \mathbf{k}') - 2\pi i \delta(E_{k''} - E_{k'}) \langle \phi_{\mathbf{k}''} | V | \phi^{(+)}_{\mathbf{k}'} \rangle. \qquad (3.18)
$$

Eqn 3.15 can also be written

$$
\begin{aligned}
S_{\mathbf{k}'',\mathbf{k}'} &= \langle \phi^{(-)}_{\mathbf{k}''} | \phi^{(+)}_{\mathbf{k}'} \rangle \\
&= \langle \phi^{(-)}_{\mathbf{k}''} | \phi^{(-)}_{\mathbf{k}'} \rangle + \langle \phi^{(-)}_{\mathbf{k}''} | \phi^{(+)}_{\mathbf{k}'} - \phi^{(-)}_{\mathbf{k}'} \rangle \qquad (3.19)
\end{aligned}
$$

which can be decomposed in the same way as eqn 3.15, giving

$$
S_{\mathbf{k}'',\mathbf{k}'} = \delta(\mathbf{k}'' - \mathbf{k}') - 2\pi i \delta(E_{k''} - E_{k'}) \langle \phi^{(-)}_{\mathbf{k}''} | V | \phi_{\mathbf{k}'} \rangle. \qquad (3.20)
$$

When substituted into eqn 3.13, this decomposition of the scattering matrix can be explained by saying the first term in eqns 3.18 and 3.20 corresponds to the probability amplitude that the component $\langle \phi_{\mathbf{k}'} | \Psi_{(in)} \rangle$ of the *in* asymptote passes the target without interacting. The second terms represent the probability amplitude that the component $|\phi_{\mathbf{k}'}\rangle$ scatters into the asymptotic momentum vector $\mathbf{k}''$. The matrix elements $\langle \phi_{\mathbf{k}''} | V | \phi^{(+)}_{\mathbf{k}'} \rangle$ and $\langle \phi^{(-)}_{\mathbf{k}''} | V | \phi_{\mathbf{k}'} \rangle$ are referred to as the *transition matrix elements*, $T_{\mathbf{k}'',\mathbf{k}'}$, and are of fundamental importance in calculating the experimentally observable differential cross section. $\langle \phi^{(-)}_{\mathbf{k}''} | V | \phi_{\mathbf{k}'} \rangle$ is referred to as the *post* form of the transition matrix and $\langle \phi_{\mathbf{k}''} | V | \phi^{(+)}_{\mathbf{k}'} \rangle$ the *prior*.

3.3 Experimental Differential Cross Sections

The quantity which is the link between experimental measurements and theoretical calculations is the *differential cross section.* Although not necessarily measured in experiments or calculated theoretically, most quantities of interest, total scattering or reactive cross sections, momentum transfer cross section etc. can be derived from the differential cross section.

Consider the basic experimental arrangement depicted in fig 3-1, where a monoenergetic beam of low mass particles impinges on a set of fixed scattering centers. Obviously this is an idealization, whose validity is derived from the assumption that the relative mass of the incident particles with respect to the targets is low. Secondly, it is assumed the internal energy of the target system is low with respect to the incident energy of the scattered particles, so the targets can be assumed to be fixed. If these assumptions are valid, the system as described is practically in it's center of mass coordinate reference system, but as shown in appendix A if the actual measurements are made in a laboratory frame moving relative to the center of mass a transformation to center of mass coordinates can always be applied.

Taking the center of the interaction volume between the incident beam and the target as the origin of the coordinate system with the z axis defined along the incident momenta $\mathbf{k_1}$, (see fig 3-2), then for a suitably performed experiment, the number of scattered particles per unit time, measured in a solid angle $d\Omega_{\hat{\mathbf{k}_2}}$, denoted $N(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1})d\Omega_{\hat{\mathbf{k}_2}}$ is

$$N(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1})d\Omega_{\hat{\mathbf{k}_2}} \propto N_s I d\Omega_{\hat{\mathbf{k}_2}}. \tag{3.21}$$

Here I is the incident flux, (the number of incident particles per unit time per unit area perpendicular to $\mathbf{k_1}$) and N_s is the number of scattering centers in the interaction volume. The proportionality constant of eqn 3.21 being the differential cross section. The unit vector $\hat{\mathbf{k_2}}$ gives the direction of the center of the solid angle $d\Omega$ with respect to the defined coordinate system. Thus

$$N(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1})d\Omega_{\mathbf{k_2}} = N_s I \frac{d\sigma}{d\Omega_{\hat{\mathbf{k}_2}}}(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1})d\Omega_{\hat{\mathbf{k}_2}}. \tag{3.22}$$

The fact that $N(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1})$ is proportional to the number of scattering centers in the interaction volume indicates that only single collision events occur. That is, once a particle

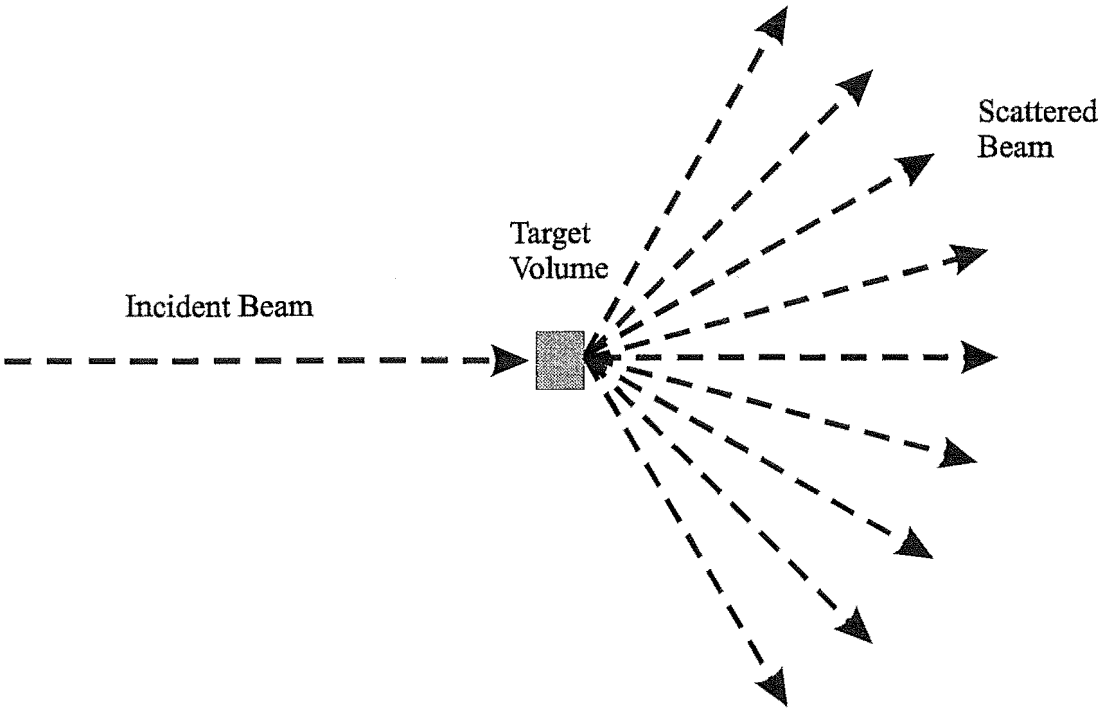


Figure 3-1: Depiction of the basic experimental scattering arrangement

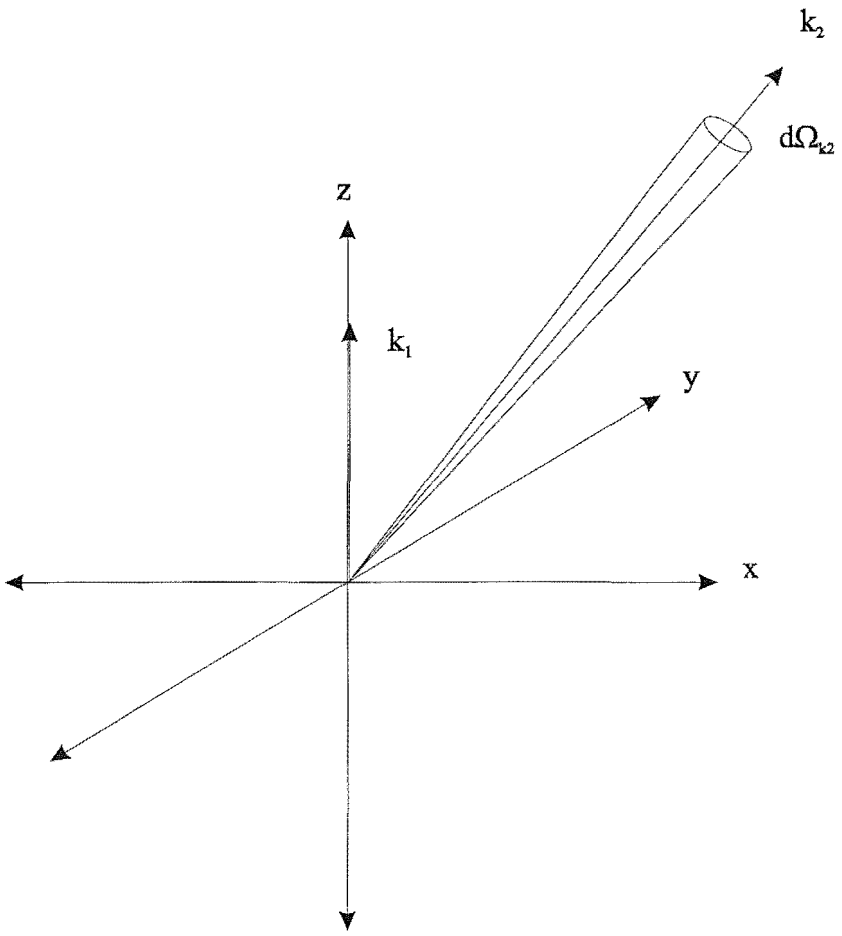


Figure 3-2: Scattering geometry in the center of mass reference frame

is scattered from one of the targets, the probability that it scatters off a second target before it leaves the interaction volume is vanishingly small. $N(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1}) \propto I$ shows there is no interference between the scattered particles.

If the probability of finding the scattered particle long after the collision, having the momentum $\mathbf{k_2}$, knowing that the incident momentum before the collision event was $\mathbf{k_1}$, is written $p(\mathbf{k_2};\mathbf{k_1})$, then evidently the probability of finding the particle with outgoing momenta in the direction of the unit vector $\hat{\mathbf{k_2}}$ is the integral over all $|\mathbf{k_2}|$ of $p(\mathbf{k_2};\mathbf{k_1})$,

$$p'(\hat{\mathbf{k_2}};\mathbf{k_1}) = \int k_2^2\, p(\mathbf{k_2};\mathbf{k_1}) dk_2. \tag{3.23}$$

Now, to fully specify the *in* asymptote, in addition to the incident momenta the impact parameter b (and θ) must be specified (see fig 3-3). The probabilities $p(\mathbf{k_2};\mathbf{k_1})$ and $p'(\hat{\mathbf{k_2}};\mathbf{k_1})$ are thus functions of the impact parameter which is expressed explicitly by writing them as $p(\mathbf{k_2};\mathbf{k_1},b,\theta)$ and $p'(\hat{\mathbf{k_2}};\mathbf{k_1},b,\theta)$. For an experiment consisting of a large number of incident particles scattered from a single target with randomly chosen b and θ, then the probability that a single particle will be detected along the outgoing vector $\hat{\mathbf{k_2}}$ must be the integral of $p'(\mathbf{k_2};\mathbf{k_1},b,\theta)$ over all b and θ. Obviously

$$N(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1}) d\Omega_{\hat{\mathbf{k}_2}} = N_s I \int db \sin\theta d\theta\, p'(\hat{\mathbf{k_2}};\mathbf{k_1},b,\theta) d\Omega_{\hat{\mathbf{k}_2}}. \tag{3.24}$$

and so from eqn 3.22 the differential cross section is

$$\frac{d\sigma}{d\Omega_{\hat{\mathbf{k}_2}}}(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1},\mathbf{b}) = \int db \sin\theta d\theta : p'(\hat{\mathbf{k_2}};\mathbf{k_1},b,\theta). \tag{3.25}$$

Additional requirements for the development of eqn 3.25 are that the volume in which the incident and target particles can interact must be point like with respect to the detection system. This means the outgoing momentum vector $\mathbf{k_2}$ is a well defined quantity. Further the variation in the differential cross section over the solid angle $d\Omega_{\hat{\mathbf{k}_2}}$ must be negligible and the interaction potential must be vanishingly small when the scattered particle is prepared and detected. Particular experimental arrangements determine whether these conditions are met in practice.

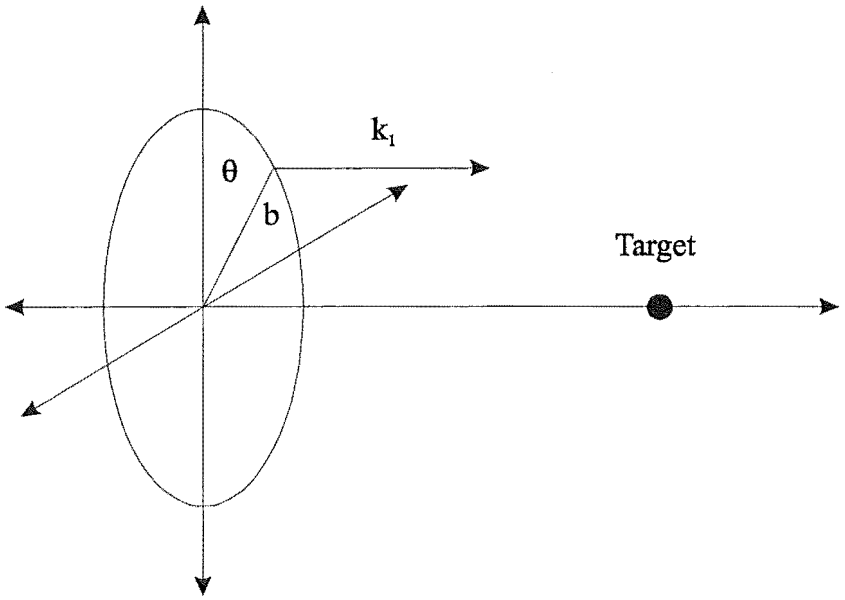


Figure 3-3: Definition of the impact parameter b

3.4 Theoretical Differential Cross Section

The probability that the outgoing particle has momenta $\mathbf{k_2}$ as $t \rightarrow \infty$ is the square of the overlap matrix $\langle \phi_{\mathbf{k_2}} | \bar{\Psi}_{(out)} \rangle$,

$$\begin{aligned} |\langle \phi_{\mathbf{k_2}} | \bar{\Psi}_{(out)} \rangle|^2 &= \left| \int S_{\mathbf{k_2},\mathbf{k'}} \psi_{\mathbf{k_1}}(\mathbf{k'}) d\mathbf{k'} \right|^2 \\ &= p(\mathbf{k_2}; \mathbf{k_1}, b, \theta) \end{aligned} \tag{3.26}$$

from eqn 3.13. Substituting this into eqn 3.23 and then into eqn 3.25 leads to the expression

$$\frac{d\sigma}{d\Omega_{\hat{\mathbf{k_2}}}}(d\Omega_{\hat{\mathbf{k_2}}} \leftarrow \mathbf{k_1}) = \int db \sin\theta d\theta \int k_2^2 \, dk_2 \left| \int S_{\mathbf{k_2},\mathbf{k'}} \psi_{\mathbf{k_1}}(\mathbf{k'}) d\mathbf{k'} \right|^2 . \tag{3.27}$$

Now making the assumption that only the scattered particles are contributing to the observed flux, the first term in eqn 3.18 or 3.20 can be dropped, and the scattering matrix is written

$$
\begin{aligned}
S_{\mathbf{k_2},\mathbf{k'}} &= -2\pi i\delta(E_{k_2} - E_{k'})\langle\phi_{\mathbf{k_2}}|V|\phi^{(+)}_{\mathbf{k'}}\rangle \\
&= -2\pi i\delta(E_{k_2} - E_{k'})\langle\phi^{(-)}_{\mathbf{k_2}}|V|\phi_{\mathbf{k'}}\rangle \\
&= \frac{i}{2\pi m}\delta(E_{k_2} - E_{k'})f(\mathbf{k_2} \leftarrow \mathbf{k'}) \qquad (3.28)
\end{aligned}
$$

$f(\mathbf{k_2} \leftarrow \mathbf{k'})$ being the *scattering amplitude*. Substituting for $S_{\mathbf{k_2},\mathbf{k'}}$ in eqn 3.27 and prudently using the delta functions [3], eqn 3.27 reduces to

$$
\frac{d\sigma}{d\Omega_{\hat{\mathbf{k_2}}}}(d\Omega_{\hat{\mathbf{k_2}}} \leftarrow \mathbf{k_1}) = \int d\mathbf{k'}\frac{k'}{k'_{\|}}|f(\mathbf{k_2} \leftarrow \mathbf{k'})\psi_{\mathbf{k_1}}(\mathbf{k'})|^2 \qquad (3.29)
$$

$k'_{\|}$ is the component of the vector $\mathbf{k'}$ parallel to the vector $\mathbf{k_1}$. The final assumption is made that the *in* asymptote's momentum distribution $\psi_{\mathbf{k_1}}(\mathbf{k})$ is sufficiently peaked about $\mathbf{k_1}$ that the term $f(\mathbf{k_2} \leftarrow \mathbf{k'})$ can be replaced by it's value at $\mathbf{k_1}$ and be taken outside the integral. Similarly it is assumed that the fraction $k'/k'_{\|}$ is sufficiently slowly varying with respect to $\psi_{\mathbf{k_1}}(\mathbf{k})$ that it can be taken as one and removed from the expression (remembering when $\mathbf{k'} = \mathbf{k_1}, k'/k'_{\|} = 1$). This gives

$$
\begin{aligned}
\frac{d\sigma}{d\Omega_{\hat{\mathbf{k_2}}}}(d\Omega_{\hat{\mathbf{k_2}}} \leftarrow \mathbf{k_1}) &= |f(\mathbf{k_2} \leftarrow \mathbf{k_1})|^2 \int d\mathbf{k'}|\psi_{\mathbf{k_1}}(\mathbf{k'})|^2 \\
&= |f(\mathbf{k_2} \leftarrow \mathbf{k_1})|^2. \qquad (3.30)
\end{aligned}
$$

This expression gives the measurable quantity $d\sigma/d\Omega_{\hat{\mathbf{k_2}}}$ as a function of the theoretically accessible scattering amplitude $f(\mathbf{k_2} \leftarrow \mathbf{k_1})$.

The two assumptions used in deriving eqn 3.30 are

1. Only particles that have interacted with scattering centers are included in the theoretical derivation. This means that comparisons between theory and experiment in the forward direction ($\mathbf{k_2} = \mathbf{k_1}$) are not meaningful, although extrapolation of experimental data to zero scattering angle is used.

2. The scattering amplitude is assumed to be a slowly varying function of $\mathbf{k}$ about $\mathbf{k_1}$,

or that the distribution of momenta in $|\Psi_{in}\rangle$ is sharply peaked about $\mathbf{k_1}$. This means experimentally, that the incident particles must be prepared with a well defined incident momenta for comparisons to be reliable.

Two broad approaches to the calculation of $f(\mathbf{k_2} \leftarrow \mathbf{k_1})$ can be employed.

- Using the expressions

$$\begin{aligned} f(\mathbf{k_2} \leftarrow \mathbf{k_1}) &= -(2\pi)^2 m \langle \phi_{\mathbf{k_2}} | V | \phi^{(+)}_{\mathbf{k_1}} \rangle \\ &= -(2\pi)^2 m \langle \phi^{(-)}_{\mathbf{k_2}} | V | \phi_{\mathbf{k_1}} \rangle \end{aligned} \tag{3.31}$$

  along with the time independent Lippmann-Schwinger equations 3.9, and applying either the variation principal or perturbation expansions to approximate the stationary scattering states.

- It can be shown that the time independent Schrödinger equation for $E > 0$

$$H|\Psi\rangle = E|\Psi\rangle \tag{3.32}$$

  has the general asymptotic solution

$$\lim_{r\to\infty} \langle \mathbf{r} | \Psi \rangle \to e^{i\mathbf{k_1}\cdot\mathbf{r}} + \frac{f(\theta,\phi)e^{ik_2 r}}{r} \tag{3.33}$$

  and the angular factor $f(\theta, \phi)$ is equal to the scattering amplitude $f(\mathbf{k_2} \leftarrow \mathbf{k_1})$. So, solving eqn 3.32 subject to the boundary condition 3.33 gives f and hence the differential cross section.

3.5 Further Remarks

As alluded to above, the whole derivation of the scattering amplitude and subsequent differential cross section can be completed without the recourse to the stationary scattering states, Lippmann-Schwinger equation or the scattering matrix.

The time independent, Schrödinger equation for the full system is

$$(H - E_k)|\phi_{\mathbf{k}}\rangle = 0. \tag{3.34}$$

The spatial representation of this equation is written

$$\begin{aligned}(H(\mathbf{r}) - E_k)\phi_{\mathbf{k}}(\mathbf{r}) &= (H_0(\mathbf{r}) + V(\mathbf{r}) - E_k)\phi_{\mathbf{k}}(\mathbf{r}) \\ &= 0 \end{aligned} \tag{3.35}$$

Now as $r \to \infty$, $V(\mathbf{r}) \to 0$ and eqn 3.35 becomes

$$(H_0(\mathbf{r}) - E_k)\phi_{\mathbf{k}}(\mathbf{r}) = \left(-\frac{1}{2}\nabla^2 - \frac{k^2}{2m}\right)\phi_{\mathbf{k}}(\mathbf{r}) = 0. \tag{3.36}$$

Changing to spherical polar coordinates with the z axis along the incident momentum vector $\mathbf{k_1}$, a separation of the radial and angular coordinates can be applied so

$$\phi_{\mathbf{k},l,m}(\mathbf{r}) = h_l^{(1)}(kr)Y_l^m(\theta,\phi), \tag{3.37}$$

$Y_l^m(\theta,\phi)$ is the usual spherical harmonic and the radial function $h_l^{(1)}(kr)$ is the Hankel function of the first kind [4]. This has the asymptotic form

$$\lim_{r\to\infty} h_l^{(1)}(kr) = \frac{1}{kr}e^{i(kr-(l+1)\pi/2)}. \tag{3.38}$$

The general solution is the sum of $\phi_{\mathbf{k},l,m}(\mathbf{r})$ over all l and m, which has the form as $r \to \infty$,

$$\begin{aligned}\lim_{r\to\infty}\sum_l\sum_m A_l\phi_{\mathbf{k},l,m}(\mathbf{r}) &= \frac{e^{ikr}}{r}\sum_l\sum_m A_l\frac{e^{-i(l+1)\pi/2}}{k}Y_l^m(\theta,\phi) \\ &= \frac{f(\theta,\phi)e^{ikr}}{r}. \end{aligned} \tag{3.39}$$

This must match the boundary condition of $\phi_{\mathbf{k}}(\mathbf{r})$ from eqn 3.35 except that $\phi_{\mathbf{k}}(\mathbf{r})$ also includes a term for the incident flux of particles along the z axis in the form of a plane wave.

Now

$$\lim_{r\to\infty} \phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k_1}\cdot\mathbf{r}} + \frac{f(\theta,\phi)e^{ikr}}{r} \tag{3.40}$$

(see eqn 3.33) and it is required to show that $f(\theta,\phi)$ is equal to the scattering amplitude from eqn 3.28.

This method of development of the scattering equations based on the time independent Schrödinger equation is widely used in scattering texts. The interpretation of the function $\phi_{\mathbf{k}}(\mathbf{r})$ is of an incoming flux of particles given by the plane wave $\exp(i\mathbf{k_1}\cdot\mathbf{r})$ and an infinite flux of outgoing spherical waves. Although this picture is simple and the derivation obvious it should be noted that the state $\phi_{\mathbf{k}}(\mathbf{r})$ is non normalizable and thus is not a proper vector in the Hilbert space of the system. Time dependent theory and the notion of wave packets are required to obtain a consistent theory. Also using the time dependent theory introduces another route to the calculation of f via the transition matrix elements and the Lippmann-Schwinger equation.

3.5.1 Inelastic Scattering

The discussion to this point has centered on potential scattering, where the target is assumed structureless. Because the internal energy of the target cannot change and we are assuming an infinitely heavy target, only elastic collisions are possible. ($|\mathbf{k_1}| = |\mathbf{k_2}|$). When inelastic collisions are possible, the derivation of the differential cross section in terms of the scattering amplitude changes slightly. For the elastic case, the energy delta function in the scattering matrix 3.28 can be written

$$\begin{aligned} \delta(E_{k_2} - E_{k'}) &= 2\delta(k_2^2 - k'^2) \\ &= 2\delta(\mathbf{k_2} - \mathbf{k'}) \end{aligned} \tag{3.41}$$

from the fact that $|\mathbf{k_2}| = |\mathbf{k'}|$. For inelastic scattering this argument must be modified. The final result is the differential cross section is given by the equation

$$\frac{d\sigma}{d\Omega_{\hat{\mathbf{k_2}}}}(d\Omega_{\hat{\mathbf{k_2}}} \leftarrow \mathbf{k_1}) = k_2 \int d\mathbf{k}' \frac{1}{k'_{\parallel}} |f(\mathbf{k_2} \leftarrow \mathbf{k}')\psi_{\mathbf{k_1}}(\mathbf{k}')|^2. \tag{3.42}$$

Making the assumption of $\psi_{\mathbf{k_1}}(\mathbf{k}')$ being sharply peaked about $\mathbf{k_1}$ (see eqn 3.29 and eqn 3.30), eqn 3.42 reduces to

$$\frac{d\sigma}{d\Omega_{\hat{\mathbf{k_2}}}}(d\Omega_{\hat{\mathbf{k_2}}} \leftarrow \mathbf{k_1}) = \frac{k_2}{k_1} |f(\mathbf{k_2} \leftarrow \mathbf{k_1})|^2. \tag{3.43}$$

3.5.2 Literature

There are a very large number of books devoted to the subject of quantum scattering theory. An excellent introductory text is *Scattering Theory* by John Taylor [3]. It covers material from basic mathematical preliminaries to multichannel scattering theory and treatment of identical particles. Another useful text is *Scattering Theory of Waves and Particles* by Roger Newton [1]. This work covers light, classical and quantum scattering. Other notable books are *The Theory of Atomic Collisions* by Mott and Massey [5] which is possibly the first comprehensive study of quantum scattering theory, *Quantum Scattering Theory for Several Particle Systems* by Faddeev and Merkuriev [6], *Quantum Theory of Scattering* by Wu and Ohmura [7] and *Quantum Theory of Scattering Processes* by Farina [8], which covers N particle systems, identical particles and some applications of the theory.

Chapter 4

Electron-Atom and Electron-Molecule Scattering

The previous two chapters give a brief introduction to the scattering of two spin-less, structureless mass points via a local interaction potential $V(\mathbf{r})$. In this chapter these ideas are extended to the actual physical process of scattering electrons from atoms and molecules.

Three important extensions of the basic equations are studied. First, the internal structure of the target must be included. Atoms and molecules contain electrons whose motions must be considered when applying the scattering equations. Electrons are fermions and so when target electrons are included, the symmetry properties of the resulting wave functions under exchange of two electrons must be correctly treated. Finally, electrons being spin 1/2 particles, the spin angular momentum of the many particle wave functions must be considered.

The question of molecular motion, vibration and rotation, is considered in chapter 8. All the discussion in the next three chapters is based on the *adiabatic nuclei* approximation, where the target nuclei are assumed fixed during the collision.

4.1 Atomic and Molecular Targets

4.1.1 H, H_0 and the Interaction Potential

The Hamiltonian for an atomic or molecular target within the Born-Oppenheimer approximation, considering only the electronic interactions is

$$\begin{aligned} H_t(\mathbf{r_1},\ldots,\mathbf{r_N}) &= H_t(\mathbf{R_N}) \\ &= \delta(\mathbf{R_N}-\mathbf{R'_N})\langle \mathbf{R_N}|H_t|\mathbf{R'_N}\rangle \\ &= -\sum_{\alpha=1}^{M}\sum_{i=1}^{N}\frac{Z_\alpha}{r_{\alpha i}} - \frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 \\ &\quad + \sum_{\alpha=1}^{M-1}\sum_{\beta>\alpha}^{M}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}. \end{aligned} \tag{4.1}$$

There are M nuclei of charge Z_α and N electrons. The set of electron coordinates $\mathbf{r_1},\ldots,\mathbf{r_N}$ is written more conveniently as $\mathbf{R_N}$. The first summation in eqn 4.1 represents the electron-nuclei coulombic attraction, the second term is the electron kinetic energy and the final two terms are the nuclei-nuclei and electron-electron coulombic repulsion terms respectively.

The Hamiltonian for the homogeneous equation H_0 is now just the kinetic energy operator of the additional electron whose coordinate is $\mathbf{r_a}$, added to H_t,

$$\begin{aligned} H_0(\mathbf{r_a};\mathbf{r_1},\ldots,\mathbf{r_N}) &= H_0(\mathbf{r_a},\mathbf{R_N}) \\ &= \delta(\mathbf{r_a}-\mathbf{r'_a})\delta(\mathbf{R_N}-\mathbf{R'_N})\langle \mathbf{r_a R_N}|H_0|\mathbf{r'_a R'_N}\rangle \\ &= H_t(\mathbf{R_N}) - \frac{1}{2}\nabla_a^2. \end{aligned} \tag{4.2}$$

Finally the full Hamiltonian for the system of target plus incident/scattered electron is simply the electronic Hamiltonian for an $N+1$ electron system in the presence of the external field produced by the M nuclei,

$$
\begin{aligned}
H(\mathbf{r_a};\mathbf{r_1},\ldots,\mathbf{r_N}) &= H(\mathbf{r_a};\mathbf{R_N}) \\
&= \delta(\mathbf{r_a}-\mathbf{r'_a})\delta(\mathbf{R_N}-\mathbf{R'_N})\langle \mathbf{r_a R_N}|H|\mathbf{r'_a R'_N}\rangle \\
&= H_0(\mathbf{r_a};\mathbf{R_N}) - \sum_{\alpha=1}^{M}\frac{Z_\alpha}{r_{\alpha a}} + \sum_{i=1}^{N}\frac{1}{r_{ia}} \\
&= H_0(\mathbf{r_a};\mathbf{R_N}) + V(\mathbf{r_a};\mathbf{R_N}). \qquad (4.3)
\end{aligned}
$$

This gives the interaction potential $V(\mathbf{r_a};\mathbf{R_N})$ defined with respect to the particular electron coordinate $\mathbf{r_a}$.

4.1.2 Excitation Channels

It is well known that the Schrödinger equation for an isolated atom or molecule has an infinite set of solutions

$$
i\frac{\partial}{\partial t}|\psi_n(t)\rangle = H_t|\psi_n(t)\rangle. \qquad (4.4)
$$

There is a infinite set of discrete bound states and a continuum of ionized states.

4.1.3 The Asymptotic States

The asymptotic states for electron atom/molecule scattering, are formed by combining the isolated target states $|\psi_n(t)\rangle$ with the free one-electron state $|\Psi_{\mathbf{k_1},(in)}(t)\rangle$ which is just the free state (with $m = 1$) from section 2.2.3. Deferring the treatment of the identical electrons for the moment, the asymptotes are simply the product of a target state and a free electron state

$$
|\Psi_{\mathbf{k_1},(in/out),n}(t)\rangle = |\Psi_{\mathbf{k_1},(in/out)}(t)\rangle|\psi_n(t)\rangle. \qquad (4.5)
$$

The states $|\Psi_{\mathbf{k_1},(in/out),n}(t)\rangle$ are solutions of the Schrödinger equation

$$
i\frac{\partial}{\partial t}|\Psi_{\mathbf{k_1},(in/out),n}(t)\rangle = H_0|\Psi_{\mathbf{k_1},(in/out),n}(t)\rangle \qquad (4.6)
$$

where H_0 is given by eqn 4.2.

Considering firstly the *out* asymptotes, if the total energy of the system of electron plus target is fixed at a value of E_s, then it is energetically possible to form an *out* asymptote with the target left in the state $|\psi_n(t)\rangle$ only if $E_n < E_s$. Asymptotes formed from these $|\psi_n(t)\rangle$ are called open channels, the energetically inaccessible states are called closed channels. Remembering the energy of a free electron is $E_k = k^2/2$ then for a given E_s the magnitude of the outgoing momentum $\mathbf{k_2}$ is fixed by the energy of the target state,

$$|\mathbf{k_2}| = \sqrt{2(E_s - E_n)}. \tag{4.7}$$

For the *in* asymptotes the energetics are the same, but generally the target is in a single state $|\psi_{n'}(t)\rangle$ and the incident electron's momentum is fixed at some initial value, $\mathbf{k_1}$, which fixes the total energy of the system, $E_s = E_{n'} + k_1^2/2$. This dictates through E_s, the possible *out* channels available to the system.

The scattering states $|\Psi^{(\pm)}_{\mathbf{k},n}(t)\rangle$ are defined as

$$\begin{aligned} |\Psi^{(\pm)}_{\mathbf{k},n}(t)\rangle &= \Omega^{\pm}|\Psi_{\mathbf{k},(in/out),n}(t)\rangle \\ &= \lim_{t\to\mp\infty} e^{iHt}e^{-iH_0t}|\Psi_{\mathbf{k},(in/out),n}(t)\rangle \end{aligned} \tag{4.8}$$

and

$$i\frac{\partial}{\partial t}|\Psi^{(\pm)}_{\mathbf{k},n}(t)\rangle = H|\Psi^{(\pm)}_{\mathbf{k},n}(t)\rangle \tag{4.9}$$

where $H = H_0 + V$.

The definitions of the stationary scattering states $|\phi^{(\pm)}_{\mathbf{k},n}\rangle$ of section 3.1 and the scattering matrix (eqn 3.14) follow. Finally the decomposition of the S matrix can be completed giving

$$\begin{aligned} S_{\mathbf{k_2},n;\mathbf{k_1},n'} &= \delta_{n,n'}\delta(\mathbf{k_2} - \mathbf{k_1}) - 2\pi i\,\delta(E - E')\langle\phi_{\mathbf{k_2}}\psi_n|V|\phi^{(+)}_{\mathbf{k_1},n'}\rangle \\ &= \delta_{n,n'}\delta(\mathbf{k_2} - \mathbf{k_1}) - 2\pi i\,\delta(E - E')\langle\phi^{(-)}_{\mathbf{k_2},n}|V|\phi_{\mathbf{k_1}}\psi_{n'}\rangle \end{aligned} \tag{4.10}$$

from which the scattering amplitude and the theoretical differential cross section can be

found as in section 3.4

4.1.4 The Multichannel Green's Functions

At this stage, the extension of the basic ideas of the previous two chapters to multichannel scattering looks simple. For a given energy there is now a set of possible asymptotic states corresponding to the particular state of the of the isolated target in the absence of the incident/scattered electron. The results of the previous chapters can be used to calculate the differential cross section for scattering from a chosen *in* channel to any of the open *out* channels.

Complications arise when considering the Green's functions for the multichannel case. The spectral representation of the two particle Green's function is (from appendix B)

$$G_0^{\pm}(E) = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|}{k^2 - k_0^2 \mp i\eta} \tag{4.11}$$

where $E = k_0^2/2$. The spatial representation of $G_0^{\pm}$ is then derived from the plane wave states $\langle \mathbf{r}|\phi_\mathbf{k}\rangle$ (see eqn B.27). For the multichannel case, the time independent homogeneous equation reads

$$(H_0 - E_{n,k})|\phi_\mathbf{k}\psi_n\rangle = 0. \tag{4.12}$$

Here $H_0 = H_t - \mathrm{k}^2/2$, ϕ_k are the plane wave states and ψ_n are the time independent target states. $E_{n,k} = E_n + k^2/2$. The states $|\phi_\mathbf{k}\psi_n\rangle$ form a complete set which spans the possible asymptotic states of the system,

$$\sum_n \int d\mathbf{k} |\phi_\mathbf{k}\psi_n\rangle\langle\phi_\mathbf{k}\psi_n| = 1 \tag{4.13}$$

so, the spectral representation of the multichannel Green's operator is

$$G_0^{\pm}(E) = \lim_{\eta \to 0^+} \sum_n \int d\mathbf{k} \frac{|\phi_\mathbf{k}\psi_n\rangle\langle\phi_\mathbf{k}\psi_n|}{k^2 - (k_0^2 - 2E_n) \mp i\eta}. \tag{4.14}$$

Expression 4.14 gives the exact, spectral representation of the multichannel Green's function but requires a summation over the infinite set of target states which is impossible in

practice. Either the summation is truncated or closure is applied to complete the summation (see section 5.3.1).

The application of the Green's function 4.14 to the Lippmann-Schwinger equations 3.9 is the same as section 3.1.1 giving an integral equation for the scattering states $|\phi^{(\pm)}_{\mathbf{k},n}\rangle$ which can then be utilized to evaluate the scattering amplitudes.

4.2 Rearrangement Channels, Exchange Scattering and the Pauli Principle

The transition matrix elements for scattering from the *in* channel defined by $\mathbf{k_1}$ and n' to the *out* channel $\mathbf{k_2}, n$ are

$$\begin{aligned} T_{\mathbf{k_2},n;\mathbf{k_1},n'} &= \langle \phi_{\mathbf{k_2},(out),n} | V | \phi^{(+)}_{\mathbf{k_1},n'} \rangle \\ &= \langle \phi^{(-)}_{\mathbf{k_2},n} | V | \phi_{\mathbf{k_1},(in),n'} \rangle \end{aligned} \tag{4.15}$$

4.2.1 The Asymptotic States

Taking the second of eqn 4.15, the set of asymptotic states $|\phi_{\mathbf{k_1},(in),n'}\rangle$ satisfying the time independent Schrödinger equation

$$(H_0 - E_{k_1,n'})|\phi_{\mathbf{k_1},(in),n'}\rangle = 0. \tag{4.16}$$

The Hamiltonian H_0 consists of the kinetic energy operator for the incident electron plus the isolated target Hamiltonian, eqn 4.1. No interaction terms or cross terms between the incident electron and the target exist. The coordinate representation of eqn 4.16 is

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r_a}} + H_t(\mathbf{R_N}) - E_{k_1,n'}\right) \phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N}) = 0. \tag{4.17}$$

$\mathbf{r_a}$ is the coordinate of the incident electron. Because the target Hamiltonian does not contain $\mathbf{r_a}$, a separation of variables can be applied and the wave function $\phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N})$ is written

$$\phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N}) = \phi_{\mathbf{k_1}}(\mathbf{r_a})\psi_{n'}(\mathbf{R_N}). \tag{4.18}$$

$\phi_{\mathbf{k_1}}(\mathbf{r_a})$ is simply the plane wave, $\exp(i\mathbf{k_1}\cdot\mathbf{r_a})$, and the wave function $\psi_{n'}(\mathbf{R_N})$ is the spatial representation of the target state $\langle\mathbf{R_N}|\psi_{n'}\rangle$. $\psi_{n'}(\mathbf{R_N})$ is the correctly antisymmetrised wave function for the N electron target, i.e.

$$\psi_{n'}(\mathbf{r_1},\ldots\mathbf{r_i},\ldots,\mathbf{r_j},\ldots,\mathbf{r_N}) = -\psi_{n'}(\mathbf{r_1},\ldots,\mathbf{r_j},\ldots,\mathbf{r_i},\ldots,\mathbf{r_N}) \tag{4.19}$$

but it will be noted that the wave function $\phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N})$ is not antisymmetric with respect to changing $\mathbf{r_a}$ with any of the N target electrons. This is a manifestation of the form of the Hamiltonian H_0 and is related to the *cluster decomposition principle* [8] which is fundamental to scattering theory. The cluster decomposition principle applies to a system of two or more clusters of particles, in which the total Hamiltonian for the system can be written $H = H_1 + H_2 + \ldots$ where H_i is the Hamiltonian for the ith cluster and no interaction terms between the clusters are present. If this is the case, the motions of the particles within a particular cluster can be determined by solving the Schrödinger equation for the isolated cluster

$$i\frac{\partial}{\partial t}|\Psi_i(t)\rangle = H_i|\Psi_i(t)\rangle, \tag{4.20}$$

independently of the other clusters. The wave function for the system as a whole is then just the product of the individual cluster wave functions,

$$|\Psi_{Sys}(t)\rangle = |\Psi_1(t)\rangle|\Psi_2(t)\rangle\ldots \tag{4.21}$$

4.2.2 The Stationary Scattering States

The scattering state $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$ is a solution of the Schrödinger equation

$$(H - E_{k_2,n})|\phi^{(-)}_{\mathbf{k_2},n}\rangle = 0, \tag{4.22}$$

the full Hamiltonian $H = H_0 + V$ containing the coulombic pairwise interactions between all the charged particles in the system. For the scattering of an electron from a target containing

N electrons, the $N+1$ electron wave function $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$ must be antisymmetric with respect to interchange of any two of the $N+1$ electrons.

It is interesting to compare the asymptotic states with the stationary scattering states. The asymptotic states are the product of an N electron antisymmetric wave function and a single coordinate wave function, the stationary scattering states are fully antisymmetric wave functions of the $N+1$ electrons. Taking the corresponding asymptotic wave function from section 4.2.1, $\phi_{\mathbf{k_1},(in),n}(\mathbf{r_a};\mathbf{R_N})$, the coordinate $\mathbf{r_a}$ is the only one to have a nonzero component as $r \rightarrow \infty$ of the form $\exp(i\mathbf{k_2}\cdot\mathbf{r_a})$. The boundary conditions for the target electrons confine the wave function to zero as the particular coordinates $\mathbf{r_j} \rightarrow \infty$. This can be written

$$\begin{aligned} \lim_{r_a\rightarrow\infty} \phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N}) &\rightarrow e^{i\mathbf{k_1}\cdot\mathbf{r_a}}\psi_{n'}(\mathbf{R_N}) \\ \lim_{r_j\rightarrow\infty} \phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N}) &\rightarrow 0. \end{aligned} \tag{4.23}$$

The spatial representation of the state $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$, given by

$$\phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_a},\mathbf{r_1},\ldots,\mathbf{r_N}) = \langle \mathbf{r_a},\mathbf{r_1},\ldots,\mathbf{r_N}|\phi^{(-)}_{\mathbf{k_2},n}\rangle, \tag{4.24}$$

can be written

$$\begin{aligned} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_a},\mathbf{r_1},\ldots,\mathbf{r_N}) &= \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_a};\mathbf{r_1},\ldots,\mathbf{r_N}) \\ &\quad -\sum_{i=1}^{N} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i};\mathbf{r_1},\ldots,\mathbf{r_a},\ldots,\mathbf{r_N}). \end{aligned} \tag{4.25}$$

The individual terms in eqn 4.25 are distinguished by their form as $r \rightarrow \infty$. The first term represents the *out* channel where the outgoing electron is the same as the incident electron. This is called direct scattering and the limits of $\phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_a};\mathbf{r_1},\ldots,\mathbf{r_N})$ as $r \rightarrow \infty$ are

$$\lim_{r_a\rightarrow\infty} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_a};\mathbf{r_1},\ldots,\mathbf{r_N}) \rightarrow e^{-i\mathbf{k_2}\cdot\mathbf{r_a}}\psi_n(\mathbf{r_1},\ldots,\mathbf{r_N})$$

$$\lim_{r_j \to \infty} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_a}; \mathbf{r_1}, \ldots, \mathbf{r_N}) \;\; \rightarrow \;\; 0. \tag{4.26}$$

It can be seen that this has the same form the *in* asymptotic wave function from eqn 4.23. The the second set of terms from eqn 4.25 have the limits

$$\begin{aligned}
\lim_{r_i \to \infty} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N}) &\rightarrow e^{-i\mathbf{k_2}\cdot\mathbf{r_i}} \psi_n(\mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N}) \\
\lim_{r_j (j \neq i) \to \infty} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N}) &\rightarrow 0 \\
\lim_{r_a \to \infty} \phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N}) &\rightarrow 0.
\end{aligned} \tag{4.27}$$

The $\phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N})$ correspond to a scattering event where the incident electron is captured by the target and one of the initially bound target electrons is ejected. This type of scattering event is called exchange scattering. The *out* channel is called a rearrangement channel of the *in* asymptote.

Because the electrons are fermions, the terms $\phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N})$ which have the incident electron exchanged with a bound electron in their *out* asymptote are of negative sign.

The Hamiltonian H_0 and interaction potential from section 4.1.1 are defined with respect to the incident/scattered electron. Thus the asymptotes of the functions $\phi^{(-)}_{\mathbf{k_2},n}(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N})$ are eigenfunctions of the Hamiltonian $H_0(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N})$ and the interaction potential is $V(\mathbf{r_i}; \mathbf{r_1}, \ldots, \mathbf{r_a}, \ldots, \mathbf{r_N})$, see section 4.1.1.

4.3 Electron Spin

Magnetic effects are not treated in this thesis, so the spin of the nuclei of the target are ignored as is spin orbit coupling. Again the *in* channel is defined as

$$\phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a}; \mathbf{R_N}) = e^{i\mathbf{k_1}\cdot\mathbf{r_a}} \psi_{n'}(\mathbf{R_N}). \tag{4.28}$$

The incident electron has a total spin angular momentum quantum number $s = 1/2$ with component in the quantization direction of $m_s = \pm 1/2$. The target is in a definite spin state characterized by the total spin angular momentum quantum number S and the component of

the spin angular momentum in the quantization direction, given by the quantum number M. The asymptote 4.28 is now

$$\phi_{\mathbf{k_1},(in),n'}(\mathbf{r_a};\mathbf{R_N}) = e^{i\mathbf{k_1}\cdot\mathbf{r_1}}\chi(a)\psi_{n',S,M}(\mathbf{R_N}), \tag{4.29}$$

$\chi(a)$ is the spin function of the electron a.

Combining the spin angular momenta of the two components gives the total spin angular momentum for the system which is conserved through the scattering event. The combined spin angular momentum is found by the usual rules for coupling angular momenta. The coupling of the total spin angular momentum give the possible spin angular momenta for the system

$$\begin{aligned} S_t &= |S-s|, |S-s+1|, \ldots, |S+s| \\ &= S \pm 1/2 \text{ (except when } S=0 \text{ where } S_t = 1/2) \end{aligned} \tag{4.30}$$

The z component of the combined spin angular momentum is simply $|M \pm 1/2|$. The combined spin angular momenta for variety of simple target spin states are,

Target	M	Incident electron	m	Electron + target	M_t
Singlet	0	Doublet	$\pm 1/2$	Doublet	$\pm 1/2$
Doublet	$\pm 1/2$	Doublet	$\pm 1/2$	Triplet	$1, 0, -1$
				Singlet	0
Triplet	$0, \pm 1$	Doublet	$\pm 1/2$	Quartet	$3/2, 1/2, -1/2, -3/2$
				Doublet	$1/2, -1/2$
			etc.		

The total spin angular momentum is conserved and thus the S_t and M_t for the *in* asymptote are conserved into the stationary scattering states and the *out* asymptote. Because the ejected electron must have $s = 1/2$ and $m = \pm 1/2$, the possible spin states of the target in the *out* asymptote are restricted to $S = S_t \pm 1/2$ (except for the case $S_t = 0$ where $S = 1/2$) and $M = M_t \pm 1/2$.

Writing the scattering amplitude for the scattering of an electron from an atom or mole-

cule as f, then there are four possible transitions for the magnetic quantum number of the incident/scattered electron, $f_{\alpha\alpha}, f_{\alpha\beta}, f_{\beta,\alpha}$ and $f_{\beta\beta}$. These correspond to an experiment where the polarization of the incident electron is prepared in a definite state and scattered electron's polarization is measured and constitutes the maximal amount of information available from an atomic scattering experiment. Typically the electron's polarization is not prepared and spin insensitive detectors are used to detect the ejected electron. The correct treatment of this situation is to average differential cross sections over the initial magnetic substates and sum over the final. Thus, for electron atom/molecule scattering

$$\frac{d\sigma}{d\Omega_{\hat{\mathbf{k}_2}}}(d\Omega_{\hat{\mathbf{k}_2}} \leftarrow \mathbf{k_1}) = \frac{1}{2}\left(|f_{\alpha\alpha}|^2 + |f_{\alpha\beta}|^2 + |f_{\beta\alpha}|^2 + |f_{\beta\beta}|^2\right). \tag{4.31}$$

4.4 Helium as an Example

To illustrate the points outlined above, the scattering of an electron from helium is studied in more detail.

Firstly, from fig 4-1, full Hamiltonian for three electron system in the presence of the helium nucleus is

$$\begin{aligned} H(\mathbf{r_a}, \mathbf{r_1}, \mathbf{r_2}) &= -\frac{1}{2}\nabla_a^2 - \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_a} - \frac{2}{r_1} - \frac{2}{r_2} \\ &\quad + \frac{1}{r_{1a}} + \frac{1}{r_{2a}} + \frac{1}{r_{12}} \end{aligned} \tag{4.32}$$

The Hamiltonian $H_0(\mathbf{r_a}; \mathbf{r_1}, \mathbf{r_2})$ in the absence of the interaction between electron a and the atom is

$$\begin{aligned} H_0(\mathbf{r_a}; \mathbf{r_1}, \mathbf{r_2}) &= -\frac{1}{2}\nabla_a^2 - \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \\ &= -\frac{1}{2}\nabla_a^2 + H_t(\mathbf{r_1}, \mathbf{r_2}) \end{aligned} \tag{4.33}$$

The interaction potential is defined as $V = H - H_0$ which can be immediately be given

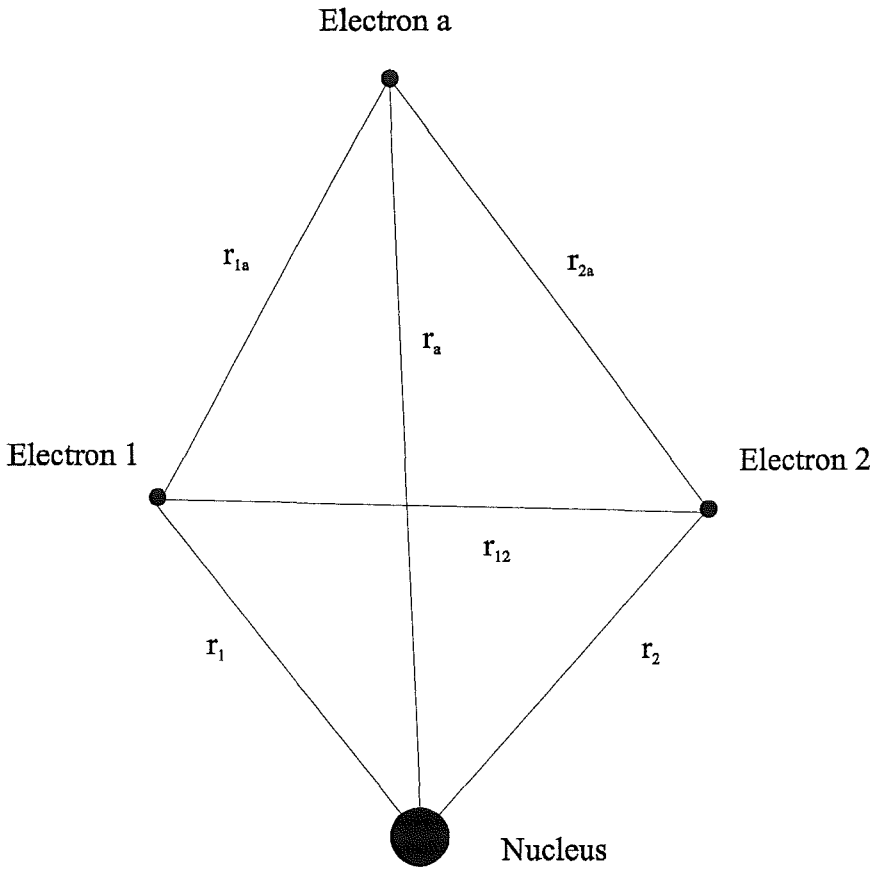


Figure 4-1: Definition of the geometry of the system of electron plus helium atom

Table 4.1: Possible singlet and triplet spin states, constructed from two spin half particles

Singlet		Triplet	
$(\alpha\beta - \beta\alpha)$	$M = 0$	$(\alpha\alpha)$	$M = 1$
		$(\alpha\beta + \beta\alpha)$	$M = 0$
		$(\beta\beta)$	$M = -1$

$$V(\mathbf{r_a}; \mathbf{r_1}, \mathbf{r_2}) = -\frac{2}{r_a} + \frac{1}{r_{1a}} + \frac{1}{r_{2a}}. \tag{4.34}$$

Now the allowable spin states of the helium atom are singlet, $M = 0$ and triplet with $M = \pm 1, 0$. The way these states are constructed from two spin half particles is given in table 4.1.

Table 4.2 gives all the possible combinations of spin states for the scattering of an electron from helium.

The term symbols for the eigenstates of He in increasing order of energy are $1^1S, 2^3S$ $2^1S, 2^3P, 2^1P, \ldots$ so for the target initially in the ground 1^1S state, energies below the threshold for excitation of the 2^3S state can only give elastic scattering. This is a case of singlet $\rightarrow$ singlet scattering, the possible spin states for this are given in table 4.2. The overall differential cross section for unpolarized electrons and spin insensitive detectors is given in eqn 4.31. In this case $f_{\alpha\beta} = f_{\beta\alpha} = 0$ and $f_{\alpha\alpha} = f_{\beta\beta}$ and so the overall differential cross section has the simple form

$$\frac{d\sigma}{d\Omega} = |f_{\alpha\alpha}|^2. \tag{4.35}$$

As the energy is raised above the threshold for excitation of the 2^3S state, $1^1S \rightarrow 2^3S$ scattering is possible. Taking the energy of the 2^3S state relative to the ground state as E_{2^3S} and the incident electron momentum vector as $\mathbf{k_1}$ then the outgoing momentum vector $\mathbf{k_2}$ has magnitude

$$k_2 = \sqrt{k_1^2 - 2E_{2^3S}}. \tag{4.36}$$

All the possible spin combinations for electron scattering from helium are given in table 4.2

Finally if the target is initially in an excited triplet state, it is possible to get triplet $\rightarrow$ triplet and triplet $\rightarrow$ singlet scattering. Also there is the possibility of scattering from an excited state

Table 4.2: Possible spin combinations for the scattering of an electron from atomic helium. *Classification* refers to direct (d) and exchange (e) scattering processes

In asymptote	*Out* asymptote		
Singlet He	Singlet He	Triplet He	Classification
$\alpha+(\alpha\beta-\beta\alpha)$	$\alpha+(\alpha\beta-\beta\alpha)$		d/e
		$\alpha+(\alpha\beta+\beta\alpha)$	d/e
		$\beta+(\alpha\alpha)$	e
$\beta+(\alpha\beta-\beta\alpha)$	$\beta+(\alpha\beta-\beta\alpha)$		d/e
		$\beta+(\alpha\beta+\beta\alpha)$	d/e
		$\alpha+(\beta\beta)$	e
Triplet He	Singlet He	Triplet He	Classification
$\alpha+(\alpha\alpha)$		$\alpha+(\alpha\alpha)$	d/e
$\alpha+(\alpha\beta+\beta\alpha)$	$\alpha+(\alpha\beta-\beta\alpha)$		d/e
		$\alpha+(\alpha\beta+\beta\alpha)$	d/e
		$\beta+(\alpha\alpha)$	e
$\alpha+(\beta\beta)$	$\beta+(\alpha\beta-\beta\alpha)$		e
		$\alpha+(\beta\beta)$	d
		$\beta+(\alpha\beta+\beta\alpha)$	e
$\beta+(\alpha\alpha)$	$\alpha+(\alpha\beta-\beta\alpha)$		e
		$\alpha+(\alpha\beta+\beta\alpha)$	e
		$\beta+(\alpha\alpha)$	d
$\beta+(\alpha\beta+\beta\alpha)$	$\beta+(\alpha\beta-\beta\alpha)$		d/e
		$\beta+(\alpha\beta+\beta\alpha)$	d/e
		$\alpha+(\beta\beta)$	e
$\beta+(\beta\beta)$		$\beta+(\beta\beta)$	d/e

to a lower energy state of the helium atom, with a corresponding increase in the energy of the ejected electron. This is called superelastic scattering.

4.5 Further Remarks

4.5.1 The Interaction Potential Including Target States

In the majority of cases, the stationary scattering state is approximated by an antisymmetrised product of $N+1$, one particle orbitals

$$|\phi^{(-)}_{\mathbf{k},n}\rangle = \mathcal{A}|u^{(-)}_{\mathbf{k},n}\phi_{n(1)},\ldots,\phi_{n(N)}\rangle \tag{4.37}$$

where $|u^{(-)}_{\mathbf{k},n}\rangle$ is a one particle state describing the motion of the free particle and the operator $\mathcal{A}$ combines u and the N bound orbitals $\phi_{n(i)}$ to form an antisymmetric wave function. Similarly the isolated target states are approximated by an antisymmetric, N orbital wave function $|\psi_{n'}\rangle = \mathcal{A}|\phi_{n'(1)},\ldots,\phi_{n'(N)}\rangle$. Making the further approximation that $|\phi^{(-)}_{\mathbf{k},n}\rangle = \mathcal{A}|u^{(-)}_{\mathbf{k},n}\psi_n\rangle$, where $|\psi_n\rangle$ is the target state n, which is again written as an antisymmetric product of the orbitals $\phi_{n(i)}$. Substituting in the post form of the transition matrix gives

$$\langle \mathcal{A}u_{\mathbf{k_2},n}\phi_{n(1)},\ldots,\phi_{n(N)}|V|\mathcal{A}\phi_{n'(1)},\ldots,\phi_{n'(N)}\rangle|\phi_{\mathbf{k_1}}\rangle = \langle u_{\mathbf{k_2},n}|V_{n,n'}|\phi_{\mathbf{k_1}}\rangle \tag{4.38}$$

Where $V_{n,n'}$ is the non-local potential experienced by a single electron impinging on the N electron target. The matrix element 4.38 must contain two terms, a one electron term associated with the interaction of the free electron with the target nuclei given by

$$\left\langle u_{\mathbf{k_2},n}\left|\sum_{\alpha=1}^{M}\frac{Z_\alpha}{r_{a\alpha}}\right|\phi_{\mathbf{k_1}}\right\rangle \tag{4.39}$$

and a two electron term representing the interaction between the free and bound electrons. The two electron component can again be broken in two, a direct and an exchange contribution. The direct term is

$$\left\langle u_{\mathbf{k_2},n}\left|\sum_{i=1}^{N}\sum_{j=1}^{N}J_{ij}\right|\phi_{\mathbf{k_1}}\right\rangle \tag{4.40}$$

The coulomb operator J_{ij} is

$$J_{ij} = \int d\tau_1 \phi_{n(i)}(\mathbf{r_1}) \frac{1}{r_{12}} \phi_{n'(j)}(\mathbf{r_1}) \tag{4.41}$$

The exchange term is

$$\left\langle u_{\mathbf{k_2},n} \left| \sum_{i=1}^{N} \sum_{j=1}^{N} K_{ij} \right| \phi_{\mathbf{k_1}} \right\rangle \tag{4.42}$$

where

$$K_{ij} = \frac{\phi_{n'(j)}(\mathbf{r_2})}{\phi_{\mathbf{k_1}}(\mathbf{r_2})} \int d\tau_1 \phi_{n(i)}(\mathbf{r_1}) \frac{1}{r_{12}} \phi_{\mathbf{k_1}(\mathbf{r_2})}. \tag{4.43}$$

The advantage of using this nomenclature is that the multiparticle scattering equations, reduce to the one particle scattering equations of chapters 2 and 3. The interaction potential in this case is non-local function of the N target electron coordinates and is called the *static exchange* potential.

4.5.2 Literature

A number of reviews of electron-atom and electron-molecule scattering are available. Burke [9] gives a good account of a number of important concepts and methods for molecular scattering. Also in that book is an introduction to electron-atom scattering by Joachain [10], which covers theoretical methods appropriate for the whole energy range. Morrison [11] and the extensive review of Lane [12], emphasize close coupling expansions and frame transform concepts. Lane's review contains a large section on the comparison between theory and experiment, and between theoretical methods. *Electronic and Ionic Impact Phenomena* by Massey and Burhop [13, 14] introduces both the theory and experimental methods in electron-atom and electron-molecule scattering. Other useful reviews of theoretical electron-atom scattering have been given by Callaway [15], and McCarthy and Weigold [16]. A second review by Burke [17], provides a good introduction to the methods available for the calculation of electron-atom, electron-ion and electron-molecule scattering and ionization, with an extensive bibliography.

Chapter 5

The Schwinger Variational Principle and Born's Approximation

The previous three chapters give a basic outline of the main points involved in a theoretical quantum treatment of electron scattering from atomic and molecular targets. This chapter introduces two methods used to calculate scattering data, Schwinger's variational principle and the Born approximation. Details of the calculations and results, using these methods for scattering from helium and molecular hydrogen are given in chapters 6 and 7. Both methods adopt a scheme where the stationary scattering states $|\phi^{(\pm)}_{\mathbf{k},n}\rangle$ are approximated in some manner, and the resulting transition matrix elements (see eqn 4.10) are calculated giving the scattering amplitude and hence the differential cross section.

Schwinger's variational principle can be expressed as either of two equations for the transition matrix elements, which are variationally stable with respect to the stationary scattering states. Expanding the stationary scattering states in a finite basis and forcing the resulting equations to be stationary with respect to the expansion coefficients leads to a practical expression for the evaluation of the transition matrix elements. This is shown to be equivalent to solving the operator equation for the transition operator by substituting a particular separable potential.

Born's approximation is based on perturbation theory and the series solution of the Lippmann-Schwinger equation in powers of the interaction potential. The Born series is expected to con-

verge for high energies and weak potentials. Because of the computational difficulties, usually only the first and possibly the second term in the series are calculated.

Both the Schwinger variational principle and the second Born approximation require the calculation of matrix elements of the multichannel Green's function. Section 5.3.1 introduces one method of approximating these matrix elements, known as the *closure approximation.*

5.1 The Schwinger Variational Principle

The post form of eqn 4.10 is

$$T_{\mathbf{k_2},n;\mathbf{k_1},n'} = \langle \phi^{(-)}_{\mathbf{k_2},n} | V | \phi_{\mathbf{k_1}} \psi_{n'} \rangle. \tag{5.1}$$

Given that the asymptotic state $|\phi_{\mathbf{k_1}}\psi_{n'}\rangle$ and the interaction potential (see section 4.1.1) are known, the variation method may be used to give an approximation to $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$ and $T_{\mathbf{k_2},n;\mathbf{k_1},n'}$. Simply constructing an approximate $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$ and finding the extrema of $T_{\mathbf{k_2},n;\mathbf{k_1},n'}$ from eqn 5.1 with respect to the variable parameters would not be useful as $T_{\mathbf{k_2},n;\mathbf{k_1},n'}$ is not stationary with respect small variations of $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$ about the exact state. Taking the exact stationary state as $|\phi^{(-)}_{\mathbf{k_2},n\,exact}\rangle$ then small variations of $|\phi^{(-)}_{\mathbf{k_2},n}\rangle$ about the exact wave function are written $|\phi^{(-)}_{\mathbf{k_2},n\,exact} + \delta\phi^{(-)}_{\mathbf{k_2},n}\rangle$. Substituting this into eqn 5.1 gives

$$\begin{aligned} T_{\mathbf{k_2},n;\mathbf{k_1},n'} &= \langle \phi^{(-)}_{\mathbf{k_2},n\,exact} + \delta\phi^{(-)}_{\mathbf{k_2},n} | V | \phi_{\mathbf{k_1}} \psi_{n'} \rangle \\ &= T_{\mathbf{k_2},n;\mathbf{k_1},n'\,exact} + \delta T_{\mathbf{k_2},n;\mathbf{k_1},n'}, \end{aligned} \tag{5.2}$$

indicating first order errors in the stationary scattering state produce first order errors in the transition matrix elements. To alleviate this problem it is first noted from the multichannel Lippmann-Schwinger equation

$$|\phi^{(+)}_{\mathbf{k_1},n'}\rangle = |\phi_{\mathbf{k_1}}\psi_{n'}\rangle + G_0^+ V |\phi^{(+)}_{\mathbf{k_1},n'}\rangle \tag{5.3}$$

that the free state $|\phi_{\mathbf{k_1}}\psi_{n'}\rangle$ can be replaced in eqn 5.1 giving

$$T_{\mathbf{k}_2,n;\mathbf{k}_1,n'} = \langle \phi^{(-)}_{\mathbf{k}_2,n'} | V - V G_0^+ V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle. \tag{5.4}$$

Schwinger [18], combined the three expressions for the transition matrix elements eqn 5.4, eqn 5.1 and the corresponding prior expression, to form two functionals which are stationary with respect to small variations of $|\phi^{(-)}_{\mathbf{k}_2,n}\rangle$ and $|\phi^{(+)}_{\mathbf{k}_1,n'}\rangle$ about their exact values. Firstly considering the expression

$$\begin{aligned} T^{(S1)}_{\mathbf{k}_2,n;\mathbf{k}_1,n'} &= \langle \phi^{(-)}_{\mathbf{k}_2,n} | V | \phi_{\mathbf{k}_1} \psi_{n'} \rangle + \langle \phi_{\mathbf{k}_2} \psi_n | V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle \\ &\quad - \langle \phi^{(-)}_{\mathbf{k}_2,n} | V - V G_0^+ V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle, \end{aligned} \tag{5.5}$$

writing the state $|\phi^{(-)}_{\mathbf{k}_2,n}\rangle$ as

$$|\phi^{(-)}_{\mathbf{k}_2,n}\rangle = |\phi^{(-)}_{\mathbf{k}_2,n,exact} + \delta\phi^{(-)}_{\mathbf{k}_2,n}\rangle \tag{5.6}$$

and substituting into eqn 5.5 gives

$$\begin{aligned} T^{(S1)}_{\mathbf{k}_2,n;\mathbf{k}_1,n'} &= \langle \phi^{(-)}_{\mathbf{k}_2,n\,exact} + \delta\phi^{(-)}_{\mathbf{k}_2,n} | V | \phi_{\mathbf{k}_1} \psi_{n'} \rangle + \langle \phi_{\mathbf{k}_2} \psi_n | V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle \\ &\quad - \langle \phi^{(-)}_{\mathbf{k}_2,n\,exact} + \delta\phi^{(-)}_{\mathbf{k}_2,n} | V - V G_0^+ V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle \\ &= T^{(S1)}_{\mathbf{k}_2,n;\mathbf{k}_1,n'}(\phi^{(-)}_{\mathbf{k}_2,n,exact}) \\ &\quad + \langle \delta\phi^{(-)}_{\mathbf{k}_2,n} | V | \left(|\phi_{\mathbf{k}_1} \psi_{n'}\rangle - |\phi^{(+)}_{\mathbf{k}_1,n'}\rangle + G_0^+ V |\phi^{(+)}_{\mathbf{k}_1,n'}\rangle \right) \\ &= T^{(S1)}_{\mathbf{k}_2,n;\mathbf{k}_1,n'}(\phi^{(-)}_{\mathbf{k}_2,n,exact}) + 0. \end{aligned} \tag{5.7}$$

from eqn 5.3. Similarly with small variations of $|\phi^{(+)}_{\mathbf{k}_1,n'}\rangle$ about the exact state. The second functional is

$$T^{(S2)}_{\mathbf{k}_2,n;\mathbf{k}_1,n'} = \frac{\langle \phi_{\mathbf{k}_2} \psi_n | V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle \langle \phi^{(-)}_{\mathbf{k}_2,n} | V | \phi_{\mathbf{k}_1} \psi_{n'} \rangle}{\langle \phi^{(-)}_{\mathbf{k}_1,n'} | V - V G_0^+ V | \phi^{(+)}_{\mathbf{k}_1,n'} \rangle} \tag{5.8}$$

which can easily be shown to be variationally stable with respect to $|\phi^{(\pm)}_{\mathbf{k},n}\rangle$.

The fractional expression $T^{(S2)}_{\mathbf{k_2},n;\mathbf{k_1},n'}$ has an advantage over eqn 5.5 in that the transition matrix elements are independent of the normalization of the functions $|\phi^{(\pm)}_{\mathbf{k},n}\rangle$.

An important difference between the variational methods in scattering theory and bound state variational theories, is that the variational scattering amplitudes are not upper or lower bounds on the exact scattering amplitudes. Bound state variational methods based on the Rayleigh ratio [19],

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}, \tag{5.9}$$

give an upper bound on the exact energy, which is very useful when comparing particular methods of calculation.

5.1.1 Separable Potentials and Basis Set Expansions

Returning to single particle potential scattering and introducing the complete orthonormal set of functions $\{f_i\}$ spanning the Hilbert space of the incident/scattered particle,

$$\sum_i |f_i\rangle\langle f_i| = 1 \tag{5.10}$$

the stationary scattering states $|\phi^{(\pm)}_{\mathbf{k}}\rangle$ can be written as a linear combination of the functions $|f_i\rangle$ [20],

$$|\phi^{(+)}_{\mathbf{k_1}}\rangle = \sum_i a_i|f_i\rangle \qquad |\phi^{(-)}_{\mathbf{k_2}}\rangle = \sum_{i'} b_{i'}|f_{i'}\rangle. \tag{5.11}$$

Substituting these into eqn 5.5 and requiring the transition matrix elements to be stationary with respect to the expansion coefficients a_i and $b_{i'}$, leads to the expressions for the coefficients

$$\begin{aligned} a_i &= \sum_{i'} \left(\langle f_{i'}|V - VG_0^+V|f_i\rangle\right)^{-1} \langle f_{i'}|V|\phi_{\mathbf{k_1}}\rangle \\ b_{i'} &= \sum_i \langle\phi_{\mathbf{k_1}}|V|f_i\rangle \left(\langle f_{i'}|V - VG_0^+V|f_i\rangle\right)^{-1} \end{aligned} \tag{5.12}$$

which, when substituted back into eqn 5.5 give

$$T_{\mathbf{k}_2;\mathbf{k}_1} = \sum_i \sum_{i'} \frac{\langle \phi_{\mathbf{k}_2} | V | f_i \rangle \langle f_{i'} | V | \phi_{\mathbf{k}_1} \rangle}{\langle f_{i'} | V - V G_0^+ V | f_i \rangle}. \tag{5.13}$$

For a given basis, calculating the appropriate matrix elements and combining as in eqn 5.13 gives the variational approximation to the transition matrix elements for the wave functions $|\phi_{\mathbf{k}}^{(\pm)}\rangle$ approximated using eqn 5.11. The same expression can be obtained by substituting the expansions into eqn 5.8 and requiring the matrix elements to be stationary with respect to a_i and $b_{i'}$.

Again using the complete set $\{f_i\}$, the spatial representation of the interaction can be written

$$\begin{aligned} V(\mathbf{r}) &= \delta(\mathbf{r} - \mathbf{r}') \langle \mathbf{r} | V | \mathbf{r}' \rangle \\ &= \delta(\mathbf{r} - \mathbf{r}') \sum_i \sum_{i'} \langle \mathbf{r} | f_i \rangle \langle f_i | V | f_{i'} \rangle \langle f_{i'} | \mathbf{r}' \rangle \\ &= \delta(\mathbf{r} - \mathbf{r}') \langle \mathbf{r} | V^s | \mathbf{r}' \rangle, \end{aligned} \tag{5.14}$$

the expansion $V^s = \sum_i \sum_{i'} |f_i\rangle \langle f_i | V | f_{i'} \rangle \langle f_{i'}|$ is called a separable potential and represents the projection of the exact potential onto the space spanned by the basis $\{f_i\}$. A second separable potential can be defined as

$$V^{s'} = \sum_i \sum_{i'} |V | f_i \rangle [D_{ii'}] \langle f_{i'} | V \tag{5.15}$$

$$[D_{ii'}]^{-1} = \langle f_{i'} | V | f_i \rangle \tag{5.16}$$

An operator equation for the transition operator $\hat{T}$ can be written (see eqn B.45)

$$\hat{T} = V - V G_0^+ \hat{T}, \tag{5.17}$$

substituting $V^{s'}$ for V and rearranging gives

$$\hat{T} = \sum_i \sum_{i'} \frac{|V|f_i\rangle\langle f_{i'}|V|}{\langle f_{i'}|V - VG_0^+V|f_i\rangle} \tag{5.18}$$

and so taking the free wave matrix elements of the operator $\hat{T}$ gives back eqn 5.13. Thus expression 5.13 can be thought of as coming from the functional 5.8 with a basis set expansion of the functions $|\phi_{\mathbf{k}}^{(\pm)}\rangle$ or equivalently from the free wave matrix elements of the operator defined in eqn 5.17 using the separable potential $V^{s'}$ from eqn 5.15. It will be noted that the boundary conditions for the functions $|\phi_{\mathbf{k}}^{(\pm)}\rangle$ are different to the boundary conditions of the interaction potential and thus it would be expected that different basis sets would be appropriate for the two approaches. It should be remembered that eqn 5.13 is an integral equation with the boundary conditions incorporated into the Green's operator. Thus the basis is only required to span the space the integrand is non zero. In the case of the stationary scattering states they are always associated with the interaction potential i.e. $V|\phi_{\mathbf{k}}^{(\pm)}\rangle$ which is called a *form factor*. Any basis used to expand the scattering states is only required to span the space where the interaction potential is non zero. Outside that region the integrand is zero through the interaction potential and does not contribute to the integral.

The Schwinger variational principle has been used for the study of nucleon-nucleon scattering and also as been applied to low energy scattering of electrons from atomic and molecular targets. At higher energies, a large number of intermediate states contribute to the Green's function which makes evaluation of the matrix elements difficult. Much of the work on application of the Schwinger variational principle to electron scattering, and photoionization, has been carried out by McKoy and coworkers [21, 22]. Their original work was based on low energy, potential scattering from simple atomic and molecular, static exchange potentials [23, 24, 25, 26, 27, 28, 29]. A number of fractional, variational expressions [30, 31, 32] and a multichannel extension of this work [33, 34] have been proposed. The *Schwinger multichannel variational method* has since been applied to a number of scattering systems [35, 36, 37, 38, 39, 40, 41, 42, 43, 44]. There has been some discussion on the stability of the Schwinger multichannel method [45, 46] and it's relation to the Kohn-type variational principles [47], linear algebraic methods [48] and *CI* optical potentials [49]. Work has also been published by Bermman and Kaldor [50, 51] on the inclusion of polarization in the Schwinger variational expression via an *ab initio* optical

potential, and by Bransden, Hewitt and Plummer [52] who use a pseudostate expansion to approximate the matrix elements of the Green's function, and subsequent T-matrix averaging [53] to remove the pesudoresonances.

5.2 The Born Series and the Born Approximation

One of the earliest treatments of theoretical scattering was completed by Born. He used an approach based on perturbation theory to obtain an approximation to the stationary scattering states $|\phi^{(\pm)}_{\mathbf{k},n}\rangle$ and through eqn 5.1 or the corresponding prior form, an approximation to the transition matrix elements.

Starting with the multichannel Lippmann-Schwinger equation

$$|\phi^{(+)}_{\mathbf{k_1},n'}\rangle = |\phi_{\mathbf{k}_1}\psi_{n'}\rangle + G_0^+ V|\phi^{(+)}_{\mathbf{k_1},n'}\rangle, \tag{5.19}$$

a formal, series solution for the stationary scattering state in powers of the interaction potential can be obtained by firstly making the approximation

$$|\phi^{(+)_1}_{\mathbf{k_1},n'}\rangle \approx |\phi_{\mathbf{k}_1}\psi_{n'}\rangle. \tag{5.20}$$

Substituting this on the right of eqn 5.19 gives

$$\begin{aligned} |\phi^{(+)_2}_{\mathbf{k_1},n'}\rangle &\approx |\phi_{\mathbf{k}}\psi_{n'}\rangle + G_0^+ V|\phi^{(+)_1}_{\mathbf{k_2},n'}\rangle \\ &= (1 + G_0^+ V)|\phi_{\mathbf{k}_1}\psi_{n'}\rangle. \end{aligned} \tag{5.21}$$

Continuing this process leads to the expression (neglecting the question of whether the expansion converges to the correct stationary scattering state)

$$|\phi^{(+)}_{\mathbf{k_1},n'}\rangle = (1 + G_0^+ V + G_0^+ V G_0^+ V + \ldots)|\phi_{\mathbf{k}_1}\psi_{n'}\rangle. \tag{5.22}$$

Substituting into the prior form of $T_{\mathbf{k_2},n;\mathbf{k_1},n'}$ gives the Born series approximation to the transition matrix element,

$$
\begin{aligned}
T_{\mathbf{k_2},n;\mathbf{k_1},n'} &= \langle \phi_{\mathbf{k_2}}\psi_n|V|\phi^{(+)}_{\mathbf{k_2},n'}\rangle \\
&= \langle \phi_{\mathbf{k_2}}\psi_n|(V + VG_0^+V + VG_0^+VG_0^+V + \ldots)|\phi_{\mathbf{k_1}}\psi_{n'}\rangle \\
&= -\frac{1}{(2\pi)^2}\left(f^{(0)}(\mathbf{k_2},n;\mathbf{k_1},n') + f^{(1)}(\mathbf{k_2},n;\mathbf{k_1},n') + \ldots\right) \qquad (5.23)
\end{aligned}
$$

The mth Born matrix element is

$$
f^{(m)}(\mathbf{k_2},n;\mathbf{k_1},n') = \langle \phi_{\mathbf{k_2}}\psi_n|V(G_0^+V)^m|\phi_{\mathbf{k_1}}\psi_{n'}\rangle. \qquad (5.24)
$$

A number of reviews of the Born series and related perturbative approximations, as applied to atomic scattering, are available [54, 55, 56, 15, 12, 57, 16]. Eqn 5.23 is a series in powers of the interaction potential V, and so is expected to converge rapidly for weak potentials or at high energies where the interaction energy is small compared to the total energy of the system. Holt and Moiseiwitsch [55] and Walters [57] discuss the convergence of the Born series. Generally, it is agreed that for simple targets and incident energies above $150eV$, the first Born approximation should give reliable results. Walters argues that the incident electron-nucleus interaction, which is singular at the nuclei, is the major reason for slow convergence of the Born series.

5.2.1 The First Born Approximation

A very widely used method is to use the approximation to the stationary scattering given in eqn 5.20. This method is called the *first Born approximation* or the *Born approximation.* The resultant scattering amplitude is

$$
f^{(0)}(\mathbf{k_2},n;\mathbf{k_1},n') = \frac{k_2}{k_1}\langle \phi_{\mathbf{k_2}}\psi_n|V|\phi_{\mathbf{k_1}}\psi_{n'}\rangle. \qquad (5.25)
$$

If the target states ψ_n and $\psi_{n'}$ are approximated by the antisymmetrised product of N orthonormal, one electron orbitals ϕ_i, eqn 5.25 simplifies to

$$
f^{(0)}(\mathbf{k_2},n;\mathbf{k_1},n') = \langle \phi_{\mathbf{k_2}}|V_{n,n'}|\phi_{\mathbf{k_1}}\rangle \qquad (5.26)
$$

(see section 4.5.1). For elastic scattering from a closed shell target with N doubly occupied molecular orbitals

$$V_{0,0}(\mathbf{r}) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{r_\alpha} + \sum_{\sigma=1}^{N} (2J_\sigma - K_\sigma) \tag{5.27}$$

J_σ and K_σ are the coulomb and exchange operators respectively for the occupied orbital σ. The potential $V_{0,0}$ is termed the static exchange potential being the potential experienced by an electron scattered from a fixed, ground state electron distribution including electron exchange.

The inelastic amplitude is

$$f^{(0)}(\mathbf{k_2}, n; \mathbf{k_1}, n') = \langle \phi_{\mathbf{k_2}} | V_{f,i} | \phi_{\mathbf{k_1}} \rangle \tag{5.28}$$

where

$$V_{f,i} = 2J_{f,i} - K_{f,i}. \tag{5.29}$$

For a transition where a target electron is excited from the orbital i to the orbital f, the coulomb operator is

$$J_{f,i} = \int d\tau_1 \phi_f(\mathbf{r_1}) \frac{1}{r_{12}} \phi_i(\mathbf{r_1}). \tag{5.30}$$

The nuclear term is zero due to the orthogonality of the initial and final states.

5.2.2 The Second Born Approximation

The second Born scattering amplitude is

$$f^{Born2}(\mathbf{k_2}, n; \mathbf{k_1}, n') = f^{(0)}(\mathbf{k_2}, n; \mathbf{k_1}, n') + f^{(1)}(\mathbf{k_2}, n; \mathbf{k_1}, n') \tag{5.31}$$

where

$$f^{(1)}(\mathbf{k_2}, n; \mathbf{k_1}, n') = \langle \phi_{\mathbf{k_2}} \psi_n | V G_0^+ V | \phi_{\mathbf{k_1}} \psi_{n'} \rangle$$

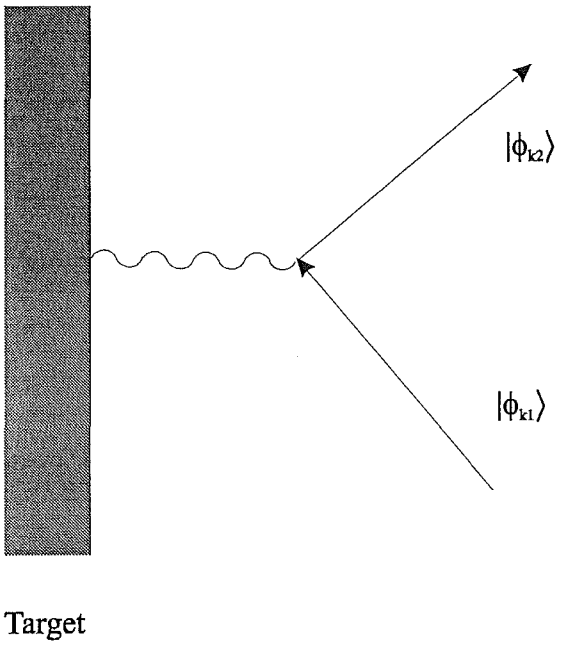


Figure 5-1: Feynman diagram representing the $f^{(0)}$ term

$$= \lim_{\eta \to 0^+} \sum_i \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi_n | V | \phi_{\mathbf{k}} \psi_i \rangle \langle \phi_{\mathbf{k}} \psi_i | V | \phi_{\mathbf{k_1}} \psi_{n'} \rangle}{k^2 - k_i^2 - i\eta} \tag{5.32}$$

from the spectral representation of the Green's operator (see section 4.1.4).

The individual terms in the Born expansion of the scattering amplitude, $f^{(0)}, f^{(1)}, \ldots$ can be represented by Feynman diagrams, which may be of use in their interpretation. The first Born amplitudes for the scattering of a particle from a fixed center of force is depicted in fig 5-1. The description of the process which leads to this term, is described as follows,

- The free particle propagates freely towards the target with momentum $\mathbf{k_1}$, the state being $|\phi_{\mathbf{k_1}}\rangle$.
- A single exchange process occurs between the incident particle and the target, with the free particle being knocked into it's final state $|\phi_{\mathbf{k_2}}\rangle$.
- The free particle propagates freely away from the target with momentum $\mathbf{k_2}$.

The second Born amplitude is represented by fig 5-2. This process is described in a similar

manner to the first Born amplitudes,

- The incident particle propagates freely towards the target in the state $|\phi_{\mathbf{k_1}}\rangle$ with incident momentum $\mathbf{k_1}$.
- A single exchange process occurs which knocks the free particle from the initial state $|\phi_{\mathbf{k_1}}\rangle$ to the intermediate state $|\phi_{\mathbf{k}}\rangle$.
- The free particle propagates freely with momentum $\mathbf{k}$.
- A second exchange process occurs which knocks he free particle from it's intermediate state $|\phi_{\mathbf{k}}\rangle$ to the final state $|\phi_{\mathbf{k_2}}\rangle$.
- The free particle propagates freely away from the target in the final state $|\phi_{\mathbf{k_2}}\rangle$.

Extension of these ideas to higher order terms is achieved simply by adding exchange events with the resulting addition of intermediate states. These concepts define a relatively simple picture of the scattering event in terms of exchange between the free particle and the target, but care must be taken to ensure that these ideas are not taken literally. The accepted view is that Feynman diagrams and indeed the perturbation expansion are simply mathematical tools, with no underlying physical reality and as such, the individual terms in the expansion of the scattering amplitude are only mathematical artifacts.

For elastic scattering ($n = n' = 0$), the first term in the summation in eqn 5.32,

$$I^{(1)}_{000} = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi_0 | V | \phi_{\mathbf{k}} \psi_0 \rangle \langle \phi_{\mathbf{k}} \psi_0 | V | \phi_{\mathbf{k_1}} \psi_0 \rangle}{k^2 - k_0^2 - i\eta} \tag{5.33}$$

gives the second order correction to the static exchange amplitude of eqn 5.26. That is for potential scattering from a structureless target with a fixed electron wave function given by $|\psi_0\rangle$, the full amplitude to second order is

$$f_{static} = f^{(0)}(\mathbf{k_2}, 0; \mathbf{k_1}, 0) + I^{(1)}_{000}. \tag{5.34}$$

The additional terms in the summation 5.32

$$I^{(1)}_{0i0} = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_1}} \psi_0 | V | \phi_{\mathbf{k}} \psi_i \rangle \langle \phi_{\mathbf{k}} \psi_i | V | \phi_{\mathbf{k_1}} \psi_0 \rangle}{k^2 - k_i^2 - i\eta} \tag{5.35}$$

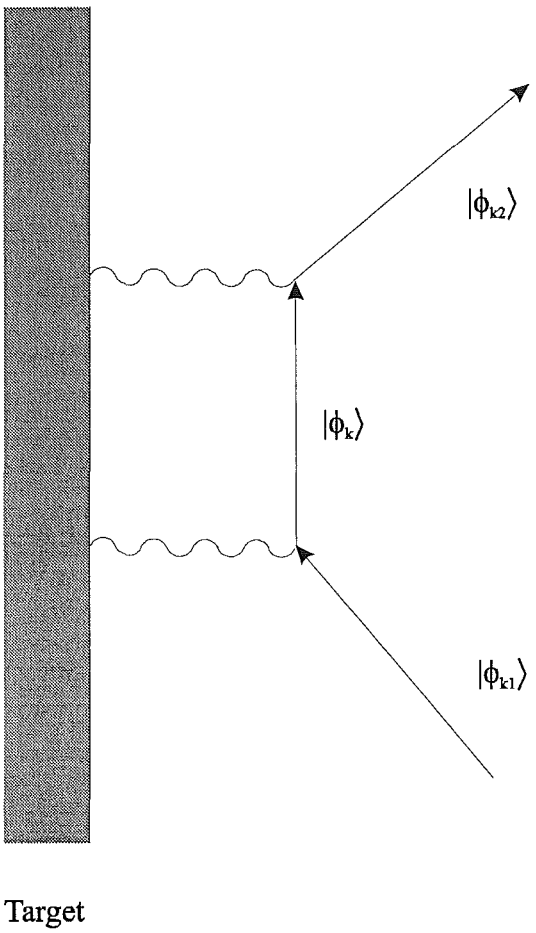


Figure 5-2: Feynman diagram representing the $f^{(1)}$ term

where $k_i^2 = k_0^2 - 2E_i$ (k_0 is the incident momentum vector relative to the ground state of the target) represent virtual excitations and decays of the target during the elastic collision event. Thus these terms couple the states of the target and allow the target to polarize due to the presence of the incident electron.

Similar remarks can be made for the inelastic amplitude. Interestingly the second Born amplitude includes elastic terms when the intermediate state is the same as either the initial or final state. In these cases the electron-nuclei interaction is present where it is completely absent from the first Born approximation.

From Cauchy's integral theorem [58], integrals of the form

$$I = \lim_{\eta \to 0+} \int_0^\infty dk \frac{F(k)}{k^2 - k_i^2 - i\eta} \tag{5.36}$$

can be reduced to a principle value integral plus the integrand evaluated at the pole

$$I = P.V. \int_0^\infty dk \frac{F(k)}{k^2 - k_i^2} + 2\pi i \frac{1}{2k_i} F(k_i) \tag{5.37}$$

P.V. indicating a principle value integral,

$$P.V. \int_0^\infty dk \frac{F(k)}{k^2 - k_i^2} = \lim_{\epsilon \to 0+} \left(\int_0^{k_i - \epsilon} dk \frac{F(k)}{k^2 - k_i^2} + \int_{k_i + \epsilon}^\infty dk \frac{F(k)}{k^2 - k_i^2} \right). \tag{5.38}$$

So the terms $I^{(1)}_{nin'}$ can be reduced to

$$\begin{aligned} I^{(1)}_{nin'} &= P.V. \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k}_2} \psi_n | V | \phi_{\mathbf{k}} \psi_i \rangle \langle \phi_{\mathbf{k}} \psi_i | V | \phi_{\mathbf{k}_1} \psi_{n'} \rangle}{k^2 - k_i^2} \\ &\quad + i\pi k_i \int d\Omega_{\mathbf{k}} \langle \phi_{\mathbf{k}_2} \psi_n | V | \phi_{\mathbf{k}} \psi_i \rangle \langle \phi_{\mathbf{k}} \psi_i | V | \phi_{\mathbf{k}_1} \psi_{n'} \rangle_{|\mathbf{k}| = k_i} \end{aligned} \tag{5.39}$$

the second term is the angular integral over the vector $\mathbf{k}$ evaluated at $|\mathbf{k}| = k_i$.

5.3 Approximations to the Multichannel Green's Operator

Both the Schwinger variational principle and the second Born approximation require the evaluation of matrix elements of the multichannel Green's operator. In it's spectral representation

the operator is

$$G_0^+ = \lim_{\eta \to 0^+} \sum_i \int d\mathbf{k} \frac{|\phi_\mathbf{k}\psi_i\rangle\langle\phi_\mathbf{k}\psi_i|}{k^2 - k_i^2 - i\eta}. \tag{5.40}$$

As mentioned, the difficulty in this is the summation over all target states i.

5.3.1 The Closure Approximation

The full expression for the multichannel Green's operator is

$$G_0^+ = \lim_{\eta \to 0^+} \sum_i \int d\mathbf{k} \frac{|\phi_\mathbf{k}\psi_i\rangle\langle\phi_\mathbf{k}\psi_i|}{k^2 - k_i^2 - i\eta}. \tag{5.41}$$

The summation over i includes both the bound and continuum states of the target. The intermediate momenta k_i, are related to the incident momenta k_1 through the target energies E_i, measured relative to the ground state, (see section 4.1.3)

$$k_i^2 = k_1^2 - 2E_i. \tag{5.42}$$

Now if exchange between the scattered electron and the target electrons is ignored, the composite states $|\phi_\mathbf{k}\psi_n\rangle$ can be written $|\phi_\mathbf{k}\rangle|\psi_n\rangle$. Eqn 5.41 becomes

$$G_0^+ = \lim_{\eta \to 0^+} \sum_i \int d\mathbf{k} \frac{|\phi_\mathbf{k}\rangle|\psi_i\rangle\langle\psi_i|\langle\phi_\mathbf{k}|}{k^2 - k_i^2 - i\eta}. \tag{5.43}$$

The set of all eigenfunctions of the Hamiltonian H_t form a complete set,

$$\sum_i |\psi_i\rangle\langle\psi_i| = 1, \tag{5.44}$$

so by eliminating the i dependence in the $1/(k^2 - k_i^2 - i\eta)$ term of eqn 5.43, the summation can be completed by using the closure properties of the target states. Replacing the intermediate momenta k_i, by an average momenta $\bar{k}$ allows the summation over i to be completed leaving G_0^+ in the form

$$G_0^+ = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|}{k^2 - \bar{k}^2 - i\eta}. \tag{5.45}$$

$\bar{k}$ can be written $\bar{k}^2 = k_1^2 - 2\Delta$ (see eqn 5.42). Δ is known as the *closure energy*. This is the basis of the closure approximation to the multichannel Greens operator. Systematic improvement on this basic approximation can be made by including explicitly a finite set of intermediate states. Inclusion of L intermediate states leaves the Green's operator as

$$G_0^+ = \sum_{l=1}^{L} \widehat{I}_b(l, k_l) - \widehat{C}(\bar{k}) \tag{5.46}$$

where the integral I_b is

$$\widehat{I}_b(l, z) = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{|\phi_\mathbf{k}\psi_l\rangle\langle\phi_\mathbf{k}\psi_l|}{k^2 - z^2 - i\eta}. \tag{5.47}$$

$\widehat{C}(\bar{k})$ represents all the remaining terms not included in the summation over l,

$$\widehat{C}(\bar{k}) = \sum_{l=1}^{L} \widehat{I}_b(l, \bar{k}) - \widehat{I}_c(\bar{k}) \tag{5.48}$$

and the closure integral $\widehat{I}_c(\bar{k})$ is simply eqn 5.45.

Choice of the Closure Energy

The closure approximation requires a closure energy, $E_c = \bar{k}^2/2$ which may be chosen arbitrarily.

Walters [57] discusses the choice of closure energy with respect to the evaluation of second Born scattering amplitudes. He concludes that the closure energy should be chosen to reflect the physics of the second Born amplitudes. The polarizability of the ground state can be shown to be [57]

$$\alpha_{00} = 2 \sum_{i \neq 0} |\langle\psi_0|Z|\psi_i\rangle|^2 / (E_n - E_0) \tag{5.49}$$

where $Z = z_1 + z_2 + \ldots + z_N$. Using the same set of states as eqn 5.46, and substituting E_c for the E_n, the correct polarizability can be achieved by varying the closure energy. Alternatively the closure energy can be chosen so that the second Born matrix elements obey the optical theorem,

$$\mathrm{Im}\left(f^{Born2}(\mathbf{k_1},\mathbf{k_1})\right) = \sum_{i=open} \frac{k_0}{4\pi}\sigma_i^{B1} \tag{5.50}$$

The integrated cross sections, σ_i^{B1} are estimated using an alternative theory or from experiment and the imaginary part of the forward cross section is evaluated using the closure approximation, the closure energy being varied until the two match.

The closure approximation has been applied to the evaluation of second Born matrix elements for scattering of electrons from atomic targets. This topic will be discussed further in the following chapter.

5.4 Further Remarks

5.4.1 Literature

There are a number of ways of theoretically treating the atomic scattering problem, with particular methods being suited to specific systems and energies. Some notable work which has not been discussed are the *R-matrix theory* [59, 60, 61], *Kohn variational method* [62, 63], the *linear algebraic approach* [64] and the *independent atom method* [65, 66]. There are also extensions of the Born ideas, such as the *distorted wave Born approximation* [67, 57] and the *Eikonal-Born series* [68, 69, 57].

Chapter 6

Electron-Helium Scattering

In this chapter, the calculations undertaken into the scattering of electrons from atomic helium are discussed. The scattering amplitudes are evaluated using the first and second Born approximation. The second Born matrix elements are calculated using the closure approximation discussed in section 5.3.1. These calculations follow the work of, Byron and Joachain [70], Holt *et al.* [71] and Buckley and Walters [72], and are used only to confirm our techniques and computer code. The original work on the closure approximation was completed by Massey and Mohr [73] who calculated elastic second Born amplitudes for simple atomic targets. This work was characterized by the fact that no intermediate states were included explicitly, and the closure energy was taken as the ground state energy. Holt and Moiseiwitsch [74] extended the original work to include a finite number of intermediate states. Their method, known as the *simplified second Born approximation*, has been applied to elastic and inelastic scattering from atomic hydrogen [74, 75, 76], helium [71, 77, 70, 78, 72, 79, 80] and neon [67], and the ionization of hydrogen [81] and helium [82].

The ground state helium wave function used by Byron and Joachain [70] is a Hartree-Fock wave function fitted by a two term Slater basis. Holt *et al.* [71] and Buckley and Walters [72] use the same ground state wave function, and the excited 2^1S and 2^1P wave functions used by Flannery [83] which were derived from the unrestricted wave functions of Goldberg and Clogston [84]. We reproduce the calculations of Byron and Joachain and also use Hartree-Fock wave functions, expanded in a basis of Gaussian functions.

The final section gives scattering amplitudes calculated via the Schwinger variational prin-

ciple, for a simple Gaussian potential, and the static exchange potential from the ground state of helium.

6.1 First Born Matrix Elements

The first Born matrix elements for scattering of an electron from atomic helium, neglecting exchange are of the form

$$f^{(0)}(\mathbf{k_2}, f; \mathbf{k_1}, i) = \langle \phi_{\mathbf{k_2}}(\tau_0)\psi_f(\tau_1, \tau_2)|V|\phi_{\mathbf{k_1}}(\tau_0)\psi_i(\tau_1, \tau_2)\rangle. \tag{6.1}$$

The vector $\mathbf{k_1}$ and $\mathbf{k_2}$ are the incident and outgoing wave vectors respectively. $|\phi_{\mathbf{k}}(\tau_0)\rangle$ are the improper plane wave functions with spatial representation

$$\phi_{\mathbf{k}}(\tau_0) = \langle \tau_0|\phi_{\mathbf{k}}(\tau_0)\rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r_0}}\alpha(0). \tag{6.2}$$

The states $\psi_i(\tau_1, \tau_2)$ and $\psi_f(\tau_1, \tau_2)$ are the initial and final states of the isolated target helium atom.

Following section 4.1.1,

$$V = V(\mathbf{r_0}, \mathbf{r_1}, \mathbf{r_2}) = -\frac{2}{\mathbf{r_0}} + \frac{1}{|\mathbf{r_1} - \mathbf{r_0}|} + \frac{1}{|\mathbf{r_2} - \mathbf{r_0}|}. \tag{6.3}$$

Elastic scattering from the 1^1S ground state of helium, is given by

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \langle \phi_{\mathbf{k_2}}(\tau_0)\psi_{1^1S}(\tau_1, \tau_2)|V|\phi_{\mathbf{k_1}}(\tau_0)\psi_{1^1S}(\tau_1, \tau_2)\rangle, \tag{6.4}$$

and $|\mathbf{k_1}| = |\mathbf{k_2}|$.

Applying Bethe's integral [54],

$$\int \frac{e^{i\mathbf{K}\cdot\mathbf{r_1}}}{|\mathbf{r_1} - \mathbf{r_2}|} d\mathbf{r_1} = 4\pi \frac{e^{i\mathbf{K}\cdot\mathbf{r_2}}}{K^2} \tag{6.5}$$

eqn 6.4 reduces to

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \frac{4\pi}{K^2} \int\int \psi^*_{1^1S}(\tau_1, \tau_2) \left(e^{i\mathbf{K}\cdot\mathbf{r_1}} + e^{i\mathbf{K}\cdot\mathbf{r_2}} - 2\right) \psi_{1^1S}(\tau_1, \tau_2) d\tau_1 d\tau_2. \tag{6.6}$$

$$\mathbf{K} = \mathbf{k_1} - \mathbf{k_2}. \tag{6.7}$$

Using, for the ground state helium wave function,

$$\psi_0(\mathbf{r_1}, \mathbf{r_2}) = \phi^{\mathrm{He}}_{1s}(\mathbf{r_1})\phi^{\mathrm{He}}_{1s}(\mathbf{r_2})[\alpha(1)\beta(2) - \alpha(2)\beta(1)], \tag{6.8}$$

expression 6.6 reduces further to

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \frac{8\pi}{K^2} \int \phi^{\mathrm{He}*}_{1s}(\mathbf{r}) \left(e^{i\mathbf{K}\cdot\mathbf{r}} - 1\right) \phi^{\mathrm{He}}_{1s}(\mathbf{r}) d\mathbf{r}. \tag{6.9}$$

Byron and Joachain [70], approximated the ground state helium $1s$ orbital by a two Slater function, Hartree-Fock orbital

$$\phi^{\mathrm{He}}_{1s}(\mathbf{r}) = \frac{1}{(4\pi)^{1/2}} \left(Ae^{-\alpha r} + Be^{-\beta r}\right) \tag{6.10}$$

$A = 2.60505, B = 2.08144, \alpha = 1.41$ and $\beta = 2.61$. The integral over $\mathbf{r}$ in eqn 6.9 can now be completed (see appendix C), giving the expression for the elastic first Born amplitudes,

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \frac{2}{K^2} \left(\frac{C}{(\gamma^2 + K^2)^2} + \frac{2D}{(\lambda^2 + K^2)^2} + \frac{E}{(\epsilon^2 + K^2)^2} - 1\right), \tag{6.11}$$

$$\begin{aligned} C = 4\alpha A^2 \quad D = 2(\alpha + \beta)AB \quad E = 4\beta B^2 \\ \gamma = 2\alpha \qquad \lambda = \alpha + \beta \qquad \epsilon = 2\beta. \end{aligned} \tag{6.12}$$

If, instead of Slater functions, Gaussian functions are used to expand the helium $1s$ orbital, eqn 6.9 can again be evaluated analytically. The basis set used consists of s Gaussians,

Table 6.1: Exponents and expansion coefficients for the approximation of the helium $1s$ orbital as given by McKoy *et al.*

α_i	$c_i^{(5)}$	$c_i^{(10)}$
0.9673(2)[1]	-0.7710(-2)	0.7720(-2)
0.1461(2)	-0.5532(-1)	0.5509(-1)
0.3304(1)	-0.2208(0)	0.2222(0)
0.8731(0)	-0.4870(0)	0.4787(0)
0.2445(0)	-0.3973(0)	0.4712(0)
0.1358(0)		-0.1867(0)
0.7547(-1)		0.2045(0)
0.4193(-1)		-0.1210(0)
0.2329(-1)		0.5459(-1)
0.1294(-1)		-0.1315(-1)

$$\phi_{1s}^{\mathrm{He}}(\mathbf{r}) = \sum_{i=1}^{M} c_i N_i e^{-\alpha_i r^2} \tag{6.13}$$

where N_i is the Gaussian normalizer,

$$N_i = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \quad \text{and} \quad c_i N_i c_j N_j = \rho_{ij} \tag{6.14}$$

where ρ_{ij} is the ijth element of the density matrix.

Table 6.1 gives a list of the exponents α_i and coefficients for the five and ten function Gaussian expansions $\phi_{1s}^{\mathrm{He}}(\mathbf{r})$ from McKoy *et al* [23]. The density matrix was calculated using a Hartree-Fock, SCF calculation. GAUSSIAN 92 [85] was used to perform a single point, SCF calculation using the specified basis.

Given the density matrix, the resultant integrals can be evaluated (see appendix C) giving

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \frac{8\pi}{K^2}\left(\sum_{i=1}^{M}\sum_{j=1}^{M}\rho_{ij}\frac{16\pi^5}{(\alpha_i\alpha_j)^{3/2}}\exp\left(-K^2\frac{\alpha_i+\alpha_j}{\alpha_i\alpha_j}\right) - 1\right). \tag{6.15}$$

Table 6.2 and fig 6-1 give the first Born matrix elements, calculated using the Byron and Joachain, helium $1s$ orbital and the two Gaussian expansions of McKoy *et al.*

[1]Digits in parenthesis denotes the power of 10 by which the number should be multiplied

Table 6.2: Elastic first Born scattering amplitudes for the scattering of electrons from helium using three basis sets for the approximation of the $1s$ orbital

K	Slater	Gaussian(5)	Gaussian(10)
0.0	-0.7915(0)	-0.7844(0)	-0.7910(0)
0.5	-0.7600(0)	-0.7546(0)	-0.7596(0)
1.0	-0.6783(0)	-0.6761(0)	-0.6784(0)
1.5	-0.5740(0)	-0.5738(0)	-0.5746(0)
2.0	-0.4710(0)	-0.4712(0)	-0.4717(0)
2.5	-0.3814(0)	-0.3817(0)	-0.3821(0)
3.0	-0.3086(0)	-0.3088(0)	-0.3091(0)
3.5	-0.2510(0)	-0.2513(0)	-0.2514(0)
4.0	-0.2061(0)	-0.2062(0)	-0.2063(0)
4.5	-0.1710(0)	-0.1710(0)	-0.1710(0)
5.0	-0.1434(0)	-0.1434(0)	-0.1434(0)
5.5	-0.1215(0)	-0.1215(0)	-0.1215(0)
6.0	-0.1040(0)	-0.1040(0)	-0.1040(0)
6.5	-0.8988(-1)	-0.8986(-1)	-0.8988(-1)
7.0	-0.7831(-1)	-0.7831(-1)	-0.7833(-1)
7.5	-0.6877(-1)	-0.6878(-1)	-0.6879(-1)
8.0	-0.6081(-1)	-0.6083(-1)	-0.6084(-1)
8.5	-0.5413(-1)	-0.5414(-1)	-0.5415(-1)
9.0	-0.4847(-1)	-0.4848(-1)	-0.4849(-1)
9.5	-0.4363(-1)	-0.4364(-1)	-0.4365(-1)
10.0	-0.3947(-1)	-0.3948(-1)	-0.3949(-1)

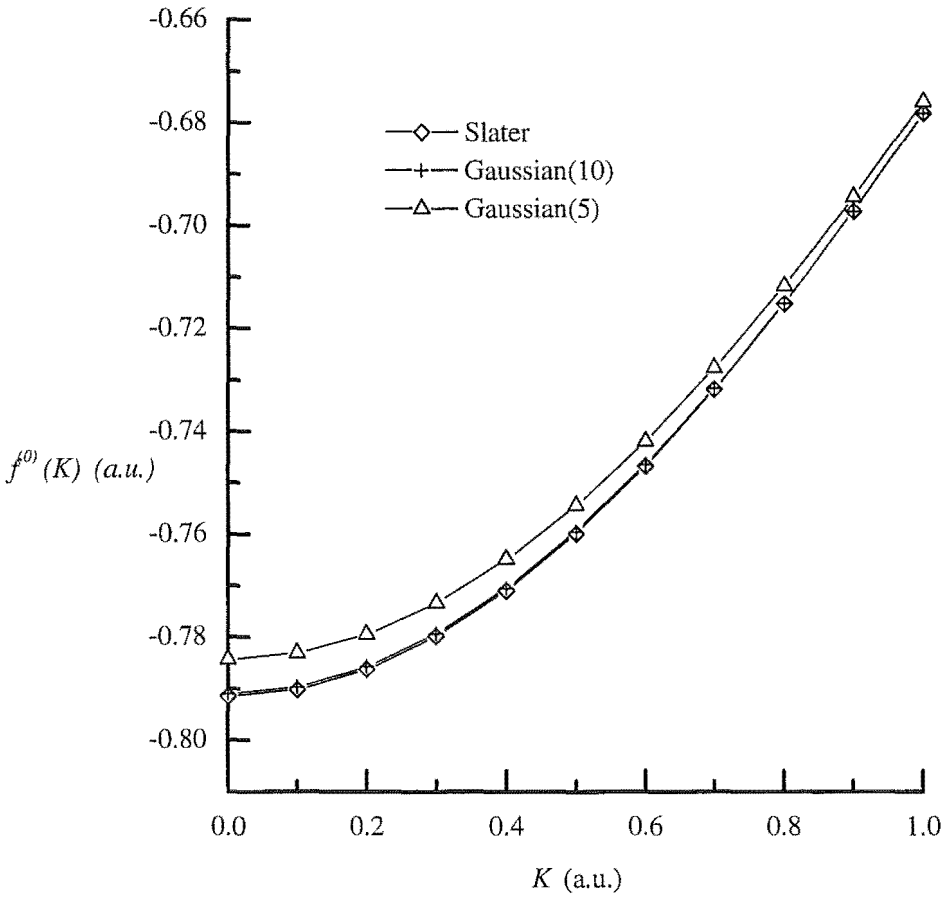


Figure 6-1: Elastic first Born helium scattering amplitudes

It can be seen that the three descriptions of the helium $1s$ orbital give very similar first Born scattering amplitudes. The discrepancy between results is more pronounced for small K, but even at $K = 0$ is not greater than 1%. The Slater results have been confirmed by the published values of Byron and Joachain.

Above $10a.u.$ the contribution to the first Born amplitudes from the electron-electron interactions becomes negligible with respect to the electron-nucleus interaction, and the three sets of results become practically indistinguishable.

6.1.1 Exchange Scattering

The first Born exchange amplitude, for scattering from the target state ψ_i to the state ψ_f, is (see sections 4.2 and 4.4)

$$f_e^{(0)}(\mathbf{k_2}, f; \mathbf{k_1}, i) = \langle \phi_{\mathbf{k_2}}(\tau_1)\psi_f(\tau_0, \tau_2)|V|\phi_{\mathbf{k_1}}(\tau_0)\psi_i(\tau_1, \tau_2)\rangle \tag{6.16}$$

Using the same orbital approximation to the ground state helium wave function as eqn 6.8, the elastic exchange amplitude reduces to

$$f_e^{(0)}(\mathbf{k_2}, 0; \mathbf{k_1}, 0) = -2f_{e1}^{(0)} + f_{e2}^{(0)} + f_{e3}^{(0)} \tag{6.17}$$

where

$$f_{e1}^{(0)} = \int \phi_{1s}^{\mathrm{He}*}(\mathbf{r_0})\frac{1}{r_0}\phi_{\mathbf{k_1}}(\mathbf{r_0})d\mathbf{r_0} \int \phi_{\mathbf{k_2}}^*(\mathbf{r_1})\phi_{1s}^{\mathrm{He}}(\mathbf{r_1})d\mathbf{r_1} \tag{6.18}$$

$$f_{e2}^{(0)} = \int\int \phi_{\mathbf{k_2}}^*(\mathbf{r_1})\phi_{1s}^{\mathrm{He}*}(\mathbf{r_1})\frac{1}{r_{01}}\phi_{\mathbf{k_1}}(\mathbf{r_0})\phi_{1s}^{\mathrm{He}}(\mathbf{r_0})d\mathbf{r_0}d\mathbf{r_1} \tag{6.19}$$

$$f_{e3}^{(0)} = \int\int \phi_{1s}^{\mathrm{He}*}(\mathbf{r_2})\phi_{1s}^{\mathrm{He}*}(\mathbf{r_2})\frac{1}{r_{02}}\phi_{\mathbf{k_1}}(\mathbf{r_0})\phi_{1s}^{\mathrm{He}}(\mathbf{r_0})d\mathbf{r_0}d\mathbf{r_2} \int \phi_{\mathbf{k_2}}^*(\mathbf{r_1})\phi_{1s}^{\mathrm{He}}(\mathbf{r_1})d\mathbf{r_1}. \tag{6.20}$$

At $300eV$ the $f_{e1}^{(0)}$ and $f_{e3}^{(0)}$ amplitudes are neglected in the treatment of Byron and Joachain because of their negligible magnitudes. Now,

Table 6.3: First Born electron-helium exchange scattering amplitudes

θ	Slater(2)	Gaussian(10)	Ochkur
0			0.9100(-1)
5	0.9244(-1)	0.9271(-1)	0.8800(-1)
10	0.8471(-1)	0.8497(-1)	0.8000(-1)
15	0.7415(-1)	0.7432(-1)	0.6900(-1)
20	0.6288(-1)	0.6295(-1)	0.5800(-1)
25	0.5231(-1)	0.5233(-1)	0.4700(-1)
30	0.4345(-1)	0.4312(-1)	0.3800(-1)
35	0.3554(-1)	0.3545(-1)	
40	0.2938(-1)	0.2932(-1)	
45	0.2445(-1)	0.2439(-1)	
50	0.2053(-1)	0.2049(-1)	
55	0.1739(-1)	0.1739(-1)	
60	0.1489(-1)	0.1492(-1)	

$$\begin{aligned} f_e^{(0)}(\mathbf{k_2},0;\mathbf{k_1},0) &\approx f_{e2}^{(0)}(\mathbf{k_2},0;\mathbf{k_1},0) \\ &= \int\int \phi^*_{\mathbf{k_2}}(\mathbf{r_1})\phi^{\mathrm{He}*}_{1s}(\mathbf{r_1})\frac{1}{r_{01}}\phi_{\mathbf{k_1}}(\mathbf{r_0})\phi^{\mathrm{He}}_{1s}(\mathbf{r_0})d\mathbf{r_0}d\mathbf{r_1} \end{aligned} \tag{6.21}$$

The integrals required for the calculation of $f_{e2}^{(0)}$, with the helium $1s$ orbital expanded in both Slater and Gaussian functions, are given in appendix D.

Table 6.3 gives the $f_{e2}^{(0)}$ terms from eqn 6.21, for $300eV$ elastic electron helium scattering calculated from the Byron and Joachain He $1s$ orbital and the 10 Gaussian approximation of McKoy *et al.* Also included are the values quoted by Byron and Joachain for the approximate $f_{e2}^{(0)}$ amplitudes calculated using the Ochkur approximation,

$$f_{e2}^{(0)} \approx -\frac{2}{k_i^2}\int e^{i\mathbf{K}\cdot\mathbf{r}}\left(\phi^{\mathrm{He}}_{1s}(\mathbf{r})\right)^2 d\mathbf{r}. \tag{6.22}$$

The two sets of results for f_{e2} are seen to be in excellent agreement. The Ochkur approximation gives results in agreement to the order of 10%. Exchange amplitudes at $200eV, 400eV$ and $500eV$ are given in table 6.4, again showing the excellent agreement between the Slater and Gaussian results.

Table 6.4: First Born exchange amplitudes for scattering at 200, 400 and 500eV

	200eV		400eV		500eV	
θ	Slater	Gaussian	Slater	Gaussian	Slater	Gaussian
5	0.1433(0)	0.1433(0)	0.6774(-1)	0.6767(-1)	0.5321(-1)	0.5176(-1)
10	0.1354(0)	0.1352(0)	0.6029(-1)	0.6039(-1)	0.4603(-1)	0.4533(-1)
15	0.1238(0)	0.1237(0)	0.5068(-1)	0.5079(-1)	0.3726(-1)	0.3689(-1)
20	0.1104(0)	0.1103(0)	0.4109(-1)	0.4114(-1)	0.2904(-1)	0.2882(-1)
25	0.9684(-1)	0.9667(-1)	0.3272(-1)	0.3273(-1)	0.2228(-1)	0.2213(-1)
30	0.8404(-1)	0.8383(-1)	0.2591(-1)	0.2590(-1)	0.1706(-1)	0.1696(-1)
35	0.7258(-1)	0.7235(-1)	0.2058(-1)	0.2059(-1)	0.1316(-1)	0.1309(-1)
40	0.6264(-1)	0.6239(-1)	0.1647(-1)	0.1636(-1)	0.1027(-1)	0.1024(-1)
45	0.5419(-1)	0.5392(-1)	0.1332(-1)	0.1334(-1)	0.8123(-2)	0.8136(-2)
50	0.4709(-1)	0.4681(-1)	0.1091(-1)	0.1095(-1)	0.6523(-2)	0.6565(-2)
55	0.4115(-1)	0.4088(-1)	0.9040(-2)	0.9113(-2)	0.5317(-2)	0.5374(-2)
60	0.3620(-1)	0.3595(-1)	0.7589(-2)	0.7679(-2)	0.4399(-2)	0.4459(-2)

6.1.2 Inelastic Scattering

The inelastic first Born matrix elements for scattering from helium are given, from eqn 6.1

$$f^{(0)}(\mathbf{k_2}, f; \mathbf{k_1}, i) = \langle \phi_{\mathbf{k_2}} \psi_f | V | \phi_{\mathbf{k_1}} \psi_i \rangle \tag{6.23}$$

where ψ_f is the final state of the target and ψ_i is the initial state which in all cases considered is the ground state of the target ψ_0.

Using the potential from eqn 6.3, and again applying Bethe's integral, (eqn 6.5), this becomes

$$\begin{aligned} f^{(0)}(\mathbf{k_2}, n; \mathbf{k_1}, 1^1S) &= \frac{4\pi}{K^2} \langle \psi_n(\mathbf{r_1}, \mathbf{r_2}) | -2 + e^{i\mathbf{K}\cdot\mathbf{r_1}} + e^{i\mathbf{K}\cdot\mathbf{r_2}} | \psi_{1^1S}(\mathbf{r_1}, \mathbf{r_2}) \rangle \\ &= \frac{4\pi}{K^2} \langle \psi_n(\mathbf{r_1}, \mathbf{r_2}) | e^{i\mathbf{K}\cdot\mathbf{r_1}} + e^{i\mathbf{K}\cdot\mathbf{r_2}} | \psi_{1^1S}(\mathbf{r_1}, \mathbf{r_2}) \rangle, \end{aligned} \tag{6.24}$$

the first term is zero because of the orthogonality of the target states. Only the direct, inelastic scattering amplitudes are considered because these are to be used in the calculation of the second Born amplitudes. The inelastic exchange amplitudes can be ignored because they provide a negligible contribution to the second Born amplitudes, with respect to the direct amplitudes. Including direct and exchange first Born amplitudes and direct second Born amplitudes means all terms in K to order -3 are included in estimating the full amplitude

[10, 74]. Only singlet $\rightarrow$ singlet inelastic scattering is possible for direct scattering events (see section 4.4).

Because the first Born amplitudes are highly peaked functions of K , the *generalised oscillator strengths* [86] are usually quoted. The generalised oscillator strength, in the length formulation is

$$f_n(K) = \frac{2E_n}{K^2} \left| \langle \psi_n(\mathbf{r_1}, \mathbf{r_2}) | e^{i\mathbf{K}\cdot\mathbf{r_1}} + e^{i\mathbf{K}\cdot\mathbf{r_2}} | \psi_0(\mathbf{r_1}, \mathbf{r_2}) \rangle \right|^2 . \tag{6.25}$$

From eqn 6.24

$$f_n(K) = \frac{E_n K^2}{8\pi^2} \left| f^{(0)}(\mathbf{k_2}, n; \mathbf{k_1}, 1^1S) \right|^2 . \tag{6.26}$$

In the limit $K \rightarrow 0$ the generalised oscillator strengths reduce to the corresponding optical oscillator strengths.

$2^1S \leftarrow 1^1S$ First Born Amplitudes

The ground state wave function $\psi_0(\mathbf{r_1}, \mathbf{r_2})$ of Byron and Joachain is given in eqn 6.8. Following Holt *et al.* [74] the 2^1S wave function is

$$\psi_{2^1S}(\mathbf{r_1}, \mathbf{r_2}) = \frac{N_{2^1S}}{\pi} \left(e^{-2r_1} \phi_{2s}(\mathbf{r_2}) + e^{-2r_2} \phi_{2s}(\mathbf{r_1}) \right) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{6.27}$$

where

$$\phi_{2s}(\mathbf{r}) = e^{-\gamma r} + Cre^{-\delta r}. \tag{6.28}$$

With $N_{2^1S} = 0.70638, C = -0.26832, \gamma = 1.1946$ and $\delta = 0.4733$, the function $\phi_{2s}(\mathbf{r})$ is a fit to the Hartree-Fock ϕ_{2s} orbital and orthogonalized to the $\phi_{1s}(\mathbf{r})$ orbital. The relative energies of the two states is given as $0.75775 a.u.$ which was taken from the accurate results of Weiss, quoted by Kim and Inokuti [86].

Substituting the functions $\psi_0(\mathbf{r_1}, \mathbf{r_2})$ and $\psi_{2^1S}(\mathbf{r_1}, \mathbf{r_2})$ in eqn 6.25 gives

Table 6.5: Gaussian orbital coefficients and expansion coefficients for the $1s$, $2s$, and frozen core $1s$ orbitals of helium

α_i	$c_i(\phi_{1s}^{He})$	$c_i(\phi_{1s}^{He^+})$	$c_i(\phi_{2s}^{He})$
0.9673(2)	-0.7720(-2)	0.9266(-2)	0.3400(-3)
0.1461(2)	-0.5510(-1)	0.6618(-1)	0.1960(-2)
0.3304(1)	-0.2222(0)	0.2953(0)	0.1174(-1)
0.8731(0)	-0.4786(0)	0.5903(0)	0.7560(-2)
0.2445(0)	-0.4707(0)	0.2367(0)	0.2333(0)
0.1358(0)	0.1853(0)	-0.7518(-1)	-0.8007(0)
0.7547(-1)	-0.2008(0)	0.2537(-1)	0.1992(1)
0.4193(-1)	0.1151(0)	-0.1892(-2)	-0.3509(1)
0.2329(-1)	-0.5081(-1)	-0.2681(-2)	0.4680(1)
0.1294(-1)	0.1215(-1)	0.1108(-2)	-0.3411(1)

$$f_{2^1S}(K)(2^1S \leftarrow 1^1S) = \frac{4E_{2^1S}}{K^2}\left|N_{2^1S}\int d\mathbf{r_1}\phi_{1s}(\mathbf{r_1})e^{i\mathbf{K}\cdot\mathbf{r_1}}\phi_{2s}(\mathbf{r_1})\right.$$
$$\left.\int d\mathbf{r_2}e^{-2r_2}\phi_{1s}(\mathbf{r_2})\right|^2. \tag{6.29}$$

Inelastic oscillator strengths or first Born amplitudes from wave functions expanded in Gaussian basis can be calculated analytically (see appendix C). The 10 function Gaussian basis of McKoy (see table 6.1) was used in a Hartree-Fock calculation to obtain an approximate $2s$ helium orbital. The frozen core $1s$ orbital of the excited state of helium was taken to be the $1s$ orbital of He^+ calculated using the same basis. Table 6.5 gives the orbital exponents and the expansion coefficients for the ground state $1s$ orbital, the $1s$ orbital of He^+ and the Hartree-Fock $2s$ orbital. An MCSCF [2] calculation was also performed with the same basis to give a second estimate of the excited state wave function. The three lowest Hartree-Fock orbitals were included as active orbitals in the multiconfigurational SCF procedure. Table 6.6 gives the expansion coefficients for the $1s$ and $2s$ orbitals generated by the MCSCF calculation.

At small values of the momentum change the oscillator strengths are highly sensitive to the orthogonality of the ground and excited states. For both the Byron and Joachain wave

[2]MCSCF (Multiconfigurational Self Consistent Field) calculations are an extension of the more usual single configuration SCF methods, which include more than one electron configuration on the SCF procedure. This type of calculation is useful for species where more than one electron configuration makes a significant contribution to the correlated wave function and for determining true excited states.

Table 6.6: Gaussian orbital coefficients and expansion coefficients for the $1s$ and $2s$ orbitals from the MCSCF calculation

α_i	$c_i(\phi_{1s}^{\mathrm{He}})$	$c_i(\phi_{2s}^{\mathrm{He}})$
0.9673(2)	0.7150(-2)	-0.6700(-3)
0.1461(2)	0.5118(-1)	0.2150(-2)
0.3304(1)	0.2214(0)	-0.2319(-1)
0.8731(0)	0.4686(0)	-0.4032(-1)
0.2445(0)	0.3685(0)	-0.2022(0)
0.1358(0)	-0.1048(0)	-0.2065(0)
0.7547(-1)	0.1050(0)	0.5466(0)
0.4193(-1)	-0.3878(0)	-0.8609(-1)
0.2329(-1)	-0.2885(0)	0.2397(1)
0.1294(-1)	-0.1449(0)	-0.2704(1)

function and the Gaussian wave functions, the excited state was Schmidt orthogonalized [87] to the ground state. Taking $\Psi_0(\mathbf{r_1},\mathbf{r_2})$ as the ground state and

$$\begin{aligned}\Psi_{2^1S}(\mathbf{r_1},\mathbf{r_2}) &= N_{2^1S}\left(\phi_{1s}^{\mathrm{He}^+}(\mathbf{r_1})\phi_{2s}^{\mathrm{He}}(\mathbf{r_2})+\phi_{1s}^{\mathrm{He}^+}(\mathbf{r_2})\phi_{2s}^{\mathrm{He}}(\mathbf{r_1})\right)\\ &\quad [\alpha(1)\beta(2)-\alpha(2)\beta(1)] \qquad (6.30)\end{aligned}$$

as the original excited state, then the excited state $\Psi_{2^1S'}(\mathbf{r_1},\mathbf{r_2})$ used in the calculation of the oscillator strengths was the orthogonalized function,

$$\Psi_{2^1S'}(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{(1-\gamma)^{1/2}}\left(\Psi_{2^1S}(\mathbf{r_1},\mathbf{r_2})-\gamma\Psi_0(\mathbf{r_1},\mathbf{r_2})\right) \qquad (6.31)$$

where $\gamma = \langle\Psi_{2^1S}(\mathbf{r_1},\mathbf{r_2})|\Psi_0(\mathbf{r_1},\mathbf{r_2})\rangle$.

Table 6.7 gives the generalised oscillator strengths for the scattering of electrons from helium from the expression eqn 6.29. The first two columns give the generalised oscillator strengths calculated using Hartree-Fock orbitals for the ground 1^1S and excited 2^1S states, the first expanded in Slater functions as described above, and the second using the 10 function, Gaussian expansion of McKoy *et al.* The third column uses the same Hartree-Fock, Gaussian ground state but the MCSCF 2^1S state expanded in the same basis. The energy difference used in this calculation was $0.7180 a.u.$ taken from the MCSCF calculation. Column four gives the quoted values of Bell *et al.* [88] calculated using the accurate, many parameter, correlated wave

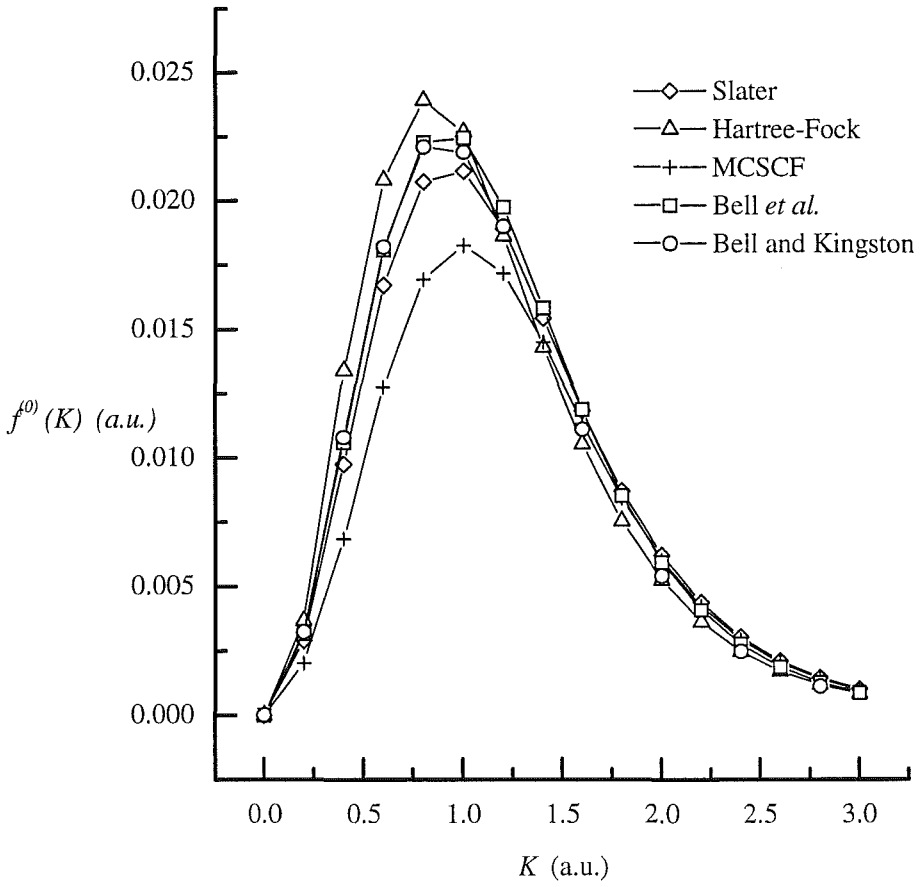


Figure 6-2: Generalised oscillator strengths for the $2^1S \leftarrow 1^1S$ transition

functions of Weiss. The final column gives the results of Bell and Kingston [89], who used Hartree-Fock functions for both the ground and excited states.

From table 6.7 and fig 6-2, the oscillator strengths, calculated using Hartree-Fock functions for the ground and excited states, match the values of Bell *et al.* well. The values calculated by Bell *et al.*, using the Weiss functions, are considered accurate and have been successfully compared with experiment. The MCSCF values do not compare as favorably with the values of Bell *et al.* A similar result has been found in calculations using accurate, correlated ground state functions and Hartree-Fock excited states [88]. This was attributed to the much smaller

Table 6.7: Generalised oscillator strengths for the $2^1S \leftarrow 1^1S$ helium transition

Ka.u.	$f_{B1(s)}$	$f_{B1(g)}$ (HF)	$f_{B1(g)}$ (MCSCF)	Bell *et al.*	Bell & Kingston
0.0	0.0000(0)	0.0000(0)	0.0000(0)	0.0000(0)	0.0000(0)
0.1	0.7561(-3)	0.8656(-3)	0.5413(-3)	0.8241(-3)	0.843(-3)
0.2	0.2894(-2)	0.3666(-2)	0.2017(-2)	0.3154(-2)	0.322(-2)
0.3	0.6059(-2)	0.8262(-2)	0.4173(-2)	0.6597(-2)	0.672(-2)
0.4	0.9755(-2)	0.1340(-1)	0.6842(-2)	0.1061(-1)	0.108(-1)
0.5	0.1346(-1)	0.1772(-1)	0.9823(-2)	0.1460(-1)	
0.6	0.1671(-1)	0.2081(-1)	0.1274(-1)	0.1808(-1)	0.182(-1)
0.7	0.1919(-1)	0.2287(-1)	0.1519(-1)	0.2070(-1)	
0.8	0.2074(-1)	0.2392(-1)	0.1693(-1)	0.2228(-1)	0.221(-1)
0.9	0.2137(-1)	0.2382(-1)	0.1794(-1)	0.2282(-1)	
1.0	0.2115(-1)	0.2267(-1)	0.1826(-1)	0.2245(-1)	0.219(-1)
1.2	0.1891(-1)	0.1863(-1)	0.1717(-1)	0.1976(-1)	0.190(-1)
1.4	0.1544(-1)	0.1429(-1)	0.1450(-1)	0.1582(-1)	
1.6	0.1184(-1)	0.1055(-1)	0.1134(-1)	0.1188(-1)	0.111(-1)
1.8	0.8701(-2)	0.7537(-2)	0.8417(-2)	0.8526(-2)	
2.0	0.6219(-2)	0.5258(-2)	0.6037(-2)	0.5946(-2)	0.541(-2)
2.2	0.4367(-2)	0.3617(-2)	0.4235(-2)	0.4074(-2)	
2.4	0.3036(-2)	0.2479(-2)	0.2936(-2)	0.2764(-2)	0.247(-2)
2.6	0.2100(-2)	0.1705(-2)	0.2027(-2)	0.1870(-2)	
2.8	0.1452(-2)	0.1181(-2)	0.1403(-2)	0.1266(-2)	0.111(-2)
3.0	0.1005(-2)	0.8260(-3)	0.9754(-3)	0.8605(-3)	
3.5	0.4080(-3)	0.3517(-3)	0.4035(-3)	0.3382(-3)	
4.0	0.1719(-3)	0.1582(-3)	0.1727(-3)	0.1406(-3)	
4.5	0.7563(-4)	0.7467(-4)	0.7658(-4)	0.6203(-4)	
5.0	0.3475(-4)	0.3675(-4)	0.3521(-4)	0.2896(-4)	
6.0	0.8303(-5)	0.9783(-5)	0.8169(-5)	0.7318(-5)	
7.0	0.2300(-5)	0.2856(-5)	0.2071(-5)	0.2169(-5)	
8.0	0.7228(-6)	0.9163(-6)	0.5738(-6)	0.7277(-6)	
9.0	0.2528(-6)	0.3274(-6)	0.1791(-6)	0.2697(-6)	
10.0	0.9681(-7)	0.1296(-6)	0.6406(-7)	0.1085(-6)	

overlap integrals between the ground and excited, Hartree-Fock states.

The generalised oscillator strengths are to be used (through the first Born amplitudes) to calculate the second Born matrix elements, (see section 5.2.2). For use as intermediate states in the calculation of matrix elements of the Green's operator, the Hartree-Fock excited states are adequate because all that is required is a complete set of states which span the Hilbert space of the system. It is not necessary to use accurate molecular excited states as intermediate states. This is a similar situation to the use of *configuration interaction* post Hartree-Fock, to extend *ab initio* bound state chemical calculations. CI calculations use virtual Hartree-Fock orbitals as additional configurations in energy minimizations.

$2^1P \leftarrow 1^1S$ First Born Amplitudes

The 2^1P state of helium consists of three magnetic substates labeled 2^1P_0 and $2^1P_{\pm 1}$. The 2^1P_m state of helium as described by Holt *et al.* is

$$\begin{aligned} \psi_{2^1P_m}(\mathbf{r_1},\mathbf{r_2}) &= \frac{N_{2^1P}}{\sqrt{\pi}}\left(e^{-2r_1}\phi_{2p_m}(\mathbf{r_2}) + e^{-2r_2}\phi_{2p_m}(\mathbf{r_1})\right) \\ &\quad [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \end{aligned} \tag{6.32}$$

where $N_{2^1P} = 0.37831$ and

$$\phi_{2p_m}(\mathbf{r}) = re^{-\lambda r}Y_{1m}(\hat{\mathbf{r}}) \qquad \lambda = 0.485. \tag{6.33}$$

This wave function was used by Flannery [83] in the investigation of the excitation of helium and was taken from the tables of atomic wave functions derived by Morse, Young and Haurwitz [90]. These wave functions are computed variationally, and include exchange. Following the arguments of section 6.1.2, the generalized oscillator strengths are

$$\begin{aligned} &f_{2^1P_m}(K)(2^1P_m \leftarrow 1^1S) = \\ &\quad \frac{4E_{2^1P}}{K^2}\left|N_{2^1P}\int d\mathbf{r_1}\phi_{1s}(\mathbf{r_1})e^{i\mathbf{K}\cdot\mathbf{r_1}}\phi_{2p_m}(\mathbf{r_1})\int d\mathbf{r_2}e^{-2r_2}\phi_{1s}(\mathbf{r_2})\right|^2. \end{aligned} \tag{6.34}$$

Table 6.8: Gaussian orbital coefficients and expansion coefficients for the $1s$,$2p$, and frozen core $1s$ orbitals of helium

	Orbital	SCF Coefficients	
Orbital	Coefficient	2 p basis	3 p basis
$1s$	0.9673(2)	0.9277(-2)	0.9279(-2)
	0.1461(2)	0.6626(-1)	0.6627(-1)
	0.3304(1)	0.2957(0)	0.2958(0)
	0.8731(0)	0.5916(0)	0.5917(0)
	0.2445(0)	0.2364(0)	0.2356(0)
	0.1358(0)	-0.7605(-1)	-0.7445(-1)
	0.7547(-1)	0.2345(-1)	0.2187(-1)
	0.4119(-1)	-0.1792(-2)	-0.9250(-3)
	0.2329(-1)	-0.3542(-2)	-0.3850(-2)
	0.1294(-1)	0.1291(-2)	0.1311(-2)
$2p$	0.3020(-1)	0.7686(0)	
	0.1230(0)	0.3391(0)	
	0.2250(-1)		0.5391(0)
	0.6930(-1)		0.4988(0)
	0.2690(0)		0.1006(0)

The required integrals are given in appendix C. The $2^1P \leftarrow 1^1S$ oscillator strengths are calculated by summing the contributions from the three substates, $m = 0, \pm 1$.

The $\phi_{1s}^{\mathrm{He}}(\mathbf{r}), \phi_{2p_m}^{\mathrm{He}}(\mathbf{r})$ and $\phi_{1s}^{\mathrm{He}^+}(\mathbf{r})$ orbitals may also be expanded in Gaussian functions. The orbitals were again calculated using a MCSCF calculation, in this case including the $1s$ and $2p$ orbitals as the active orbitals. Two p function and three p function basis sets were used, the orbital coefficients being given in table 6.8 as well as the MCSCF coefficients for the $1s$ and $2p$ orbitals. In this case the $1s$ orbital of helium was included in the SCF calculation. The 2^1P energies used in eqn 6.34, for the Gaussian calculations were $0.740268 a.u.$ for the two p basis and $0.739216 a.u.$ for the three p basis. These were taken from the energy difference between the $1s2p$ states and the Hartree-Fock, ground state.

Table 6.9 and fig 6-3 give the generalised oscillator strengths for the $2^1P \leftarrow 1^1S$ transition for the two helium wave functions described, and the results of Bell *et al.* The agreement between the four sets of results is reasonable. The f_{2^1P} calculated from the Gaussian orbitals are somewhat smaller than the corresponding Slater oscillator strengths. They also fall off faster at large K. The three p function, Gaussian orbital performs slightly better than the two p orbital, so it would be useful to repeat the calculations with an extended p function basis to

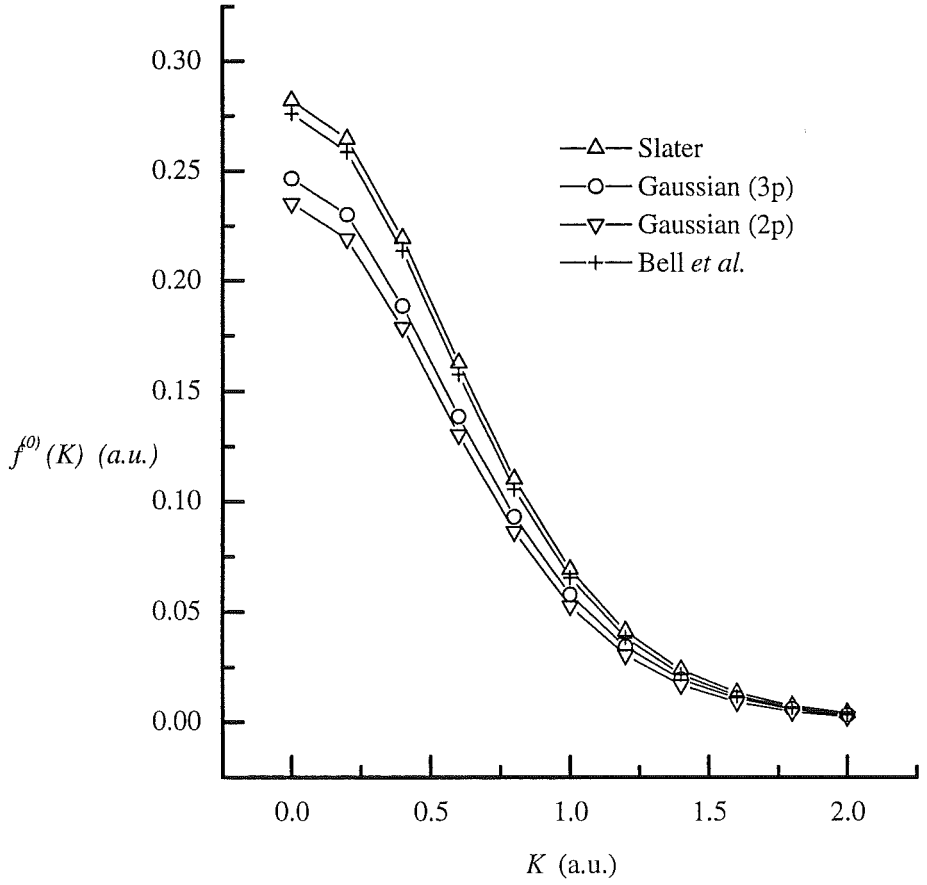


Figure 6-3: Generalised oscillator strengths for the $2^1P \leftarrow 1^1S$ transition

determine whether the basis used are giving an adequate description of the $2p$ orbital for the required calculation.

6.2 Evaluation of Second Born Matrix Elements

Second Born amplitudes for helium scattering, have been calculated within the closure approximation (see section 5.3.1). Again, the calculations follow the work of Byron and Joachain, Holt *et al.* and Buckley and Walters, and have been used to verify the numerical procedures used.

Using eqn 5.46 from section 5.3.1, the second Born matrix element, within the closure

Table 6.9: Generalised oscillator strengths for the $2^1P \leftarrow 1^1S$ helium transition

Ka.u.	$f_{B1(s)}$	MCSCF $f^{(0)}(3p)$	MCSCF $f^{(0)}(2p)$	Bell *et al.*
0.0	0.2819(0)	0.2464(0)	0.2350(0)	0.2759(0)
0.1	0.2774(0)	0.2422(0)	0.2309(0)	0.2714(0)
0.2	0.2645(0)	0.2301(0)	0.2190(0)	0.2585(0)
0.3	0.2444(0)	0.2115(0)	0.2010(0)	0.2386(0)
0.4	0.2194(0)	0.1886(0)	0.1788(0)	0.2137(0)
0.5	0.1915(0)	0.1637(0)	0.1546(0)	0.1860(0)
0.6	0.1628(0)	0.1386(0)	0.1302(0)	0.1576(0)
0.7	0.1353(0)	0.1148(0)	0.1071(0)	0.1304(0)
0.8	0.1101(0)	0.9294(-1)	0.8616(-1)	0.1055(0)
0.9	0.8799(-1)	0.7391(-1)	0.6793(-1)	0.8379(-1)
1.0	0.6921(-1)	0.5784(-1)	0.5263(-1)	0.6543(-1)
1.2	0.4124(-1)	0.3412(-1)	0.3028(-1)	0.3831(-1)
1.4	0.2372(-1)	0.1941(-1)	0.1669(-1)	0.2156(-1)
1.6	0.1337(-1)	0.1075(-1)	0.8899(-2)	0.1183(-1)
1.8	0.7468(-2)	0.5843(-2)	0.4633(-2)	0.6403(-2)
2.0	0.4170(-2)	0.3146(-2)	0.2386(-2)	0.3449(-2)
2.2	0.2342(-2)	0.1698(-2)	0.1234(-2)	0.1861(-2)
2.4	0.1329(-2)	0.9259(-3)	0.6487(-3)	0.1010(-2)
2.6	0.7631(-3)	0.5120(-3)	0.3483(-3)	0.5542(-3)
2.8	0.4444(-3)	0.2868(-3)	0.1909(-3)	0.3078(-3)
3.0	0.2626(-3)	0.1623(-3)	0.1064(-3)	0.1735(-3)
3.5	0.7522(-4)	0.4042(-4)	0.2586(-4)	0.4430(-4)
4.0	0.2355(-4)	0.1074(-4)	0.6761(-5)	0.1256(-4)
4.5	0.8001(-5)	0.3219(-5)	0.2019(-5)	0.3949(-5)
5.0	0.2925(-5)	0.1121(-5)	0.7133(-6)	0.1370(-5)
6.0	0.4730(-6)	0.1862(-6)	0.1222(-6)	0.2134(-6)
7.0	0.9455(-7)	0.3461(-7)	0.2267(-7)	0.4377(-7)
8.0	0.2246(-7)	0.6696(-8)	0.4339(-8)	0.1100(-7)
9.0	0.6146(-8)	0.1561(-8)	0.1014(-8)	0.3216(-8)
10.0	0.1893(-8)	0.4883(-9)	0.3218(-9)	0.1057(-8)

approximation is

$$f^{(1)}(\mathbf{k_2}, f; \mathbf{k_1}, i) = \sum_{n=0}^{N} I_b(n, k_n) - C(\bar{k}), \tag{6.35}$$

where $I_b(n, k_n)$ is (from eqn 5.47)

$$I_b(n, k_n) = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi_f | V | \phi_{\mathbf{k}} \psi_n \rangle \langle \phi_{\mathbf{k}} \psi_n | V | \phi_{\mathbf{k_1}} \psi_i \rangle}{k^2 - k_n^2 - i\eta} \tag{6.36}$$

and

$$C(\bar{k}) = \sum_{n=0}^{N} I_b(n, \bar{k}) - I_c(\bar{k}). \tag{6.37}$$

The closure energy is Δ so that $\bar{k}^2 = k_1^2 - 2\Delta$, and the closure integral $I_c(\bar{k})$ is written

$$I_c(\bar{k}) = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \psi_f | \langle \phi_{\mathbf{k_2}} | V | \phi_{\mathbf{k}} \rangle \langle \phi_{\mathbf{k}} | V | \phi_{\mathbf{k_1}} \rangle | \psi_i \rangle}{k^2 - \bar{k}^2 - i\eta}. \tag{6.38}$$

Following Byron and Joachain [70], the elastic scattering amplitude ($f = i = 0$) with the summation in eqn 6.35 truncated at $N = 0$ is

$$\begin{aligned} f^{(1)}(\mathbf{k_2}, 0; \mathbf{k_1}, 0) &= I_b(0, k_0) - I_b(0, \bar{k}) + I_c(\bar{k}) \\ &= \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi_0 | V | \phi_{\mathbf{k}} \psi_0 \rangle \langle \phi_{\mathbf{k}} \psi_0 | V | \phi_{\mathbf{k_1}} \psi_0 \rangle}{k^2 - k_0^2 - i\eta} \\ &\quad - \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi_0 | V | \phi_{\mathbf{k}} \psi_0 \rangle \langle \phi_{\mathbf{k}} \psi_0 | V | \phi_{\mathbf{k_1}} \psi_0 \rangle}{k^2 - \bar{k}^2 - i\eta} \\ &\quad + \lim_{\eta \to 0^+} \int \frac{\langle \psi_0 | \langle \phi_{\mathbf{k_2}} | V | \phi_{\mathbf{k}} \rangle \langle \phi_{\mathbf{k}} | V | \phi_{\mathbf{k_1}} \rangle | \psi_0 \rangle}{k^2 - \bar{k}^2 - i\eta}. \end{aligned} \tag{6.39}$$

ψ_0 being the ground state, target wave function.

For helium scattering, the ground state wave function is approximated by

$$\psi_0(\mathbf{r_1}, \mathbf{r_2}) \approx \phi_{1s}^{\mathrm{He}}(\mathbf{r_1}) \phi_{1s}^{\mathrm{He}}(\mathbf{r_2}) [\alpha(1)\beta(2) - \alpha(2)\beta(1)], \tag{6.40}$$

and the first Born matrix elements are, from eqn 6.9,

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \frac{8\pi}{K^2}\langle\phi_{1s}^{\mathrm{He}}(\mathbf{r}) \mid e^{i\mathbf{K}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}(\mathbf{r})\rangle. \tag{6.41}$$

Substituting this into eqn 6.39 gives

$$\begin{aligned}
f^{(1)}(\mathbf{k_2}, 0; \mathbf{k_1}, 0) = & \\
& 16\pi^2 \left(\lim_{\eta\to 0^+} \int \frac{4d\mathbf{k}}{K_1^2 K_2^2 (k^2 - k_0^2 - i\eta)} \langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_2}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}\rangle\langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_1}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}\rangle \right. \\
& - \lim_{\eta\to 0^+} \int \frac{4d\mathbf{k}}{K_1^2 K_2^2 (k^2 - \bar{k}^2 - i\eta)} \langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_2}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}\rangle\langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_1}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}\rangle \\
& \left. + \lim_{\eta\to 0^+} \int \frac{2d\mathbf{k}}{K_1^2 K_2^2 (k^2 - \bar{k}^2 - i\eta)} \langle\phi_{1s}^{\mathrm{He}}|(e^{i\mathbf{K_2}\cdot\mathbf{r}} - 1)(e^{i\mathbf{K_1}\cdot\mathbf{r}} - 1)|\phi_{1s}^{\mathrm{He}}\rangle \right) \\
= \; & 16\pi^2 \left(\lim_{\eta\to 0^+} \int \frac{4d\mathbf{k}}{(k^2 - k_0^2 - i\eta)} f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k}, 1^1S) f^{(0)}(\mathbf{k}, 1^1S; \mathbf{k_1}, 1^1S) \right. \\
& - \lim_{\eta\to 0^+} \int \frac{2d\mathbf{k}}{(k^2 - \bar{k}^2 - i\eta)} f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k}, 1^1S) f^{(0)}(\mathbf{k}, 1^1S; \mathbf{k_1}, 1^1S) \\
& + \lim_{\eta\to 0^+} \int \frac{2d\mathbf{k}}{(k^2 - \bar{k}^2 - i\eta)} \left(\frac{K^2}{K_1^2 K_2^2} f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) \right. \\
& \left. \left. - \frac{1}{K_1^2} f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k}, 1^1S) - \frac{1}{K_2^2} f^{(0)}(\mathbf{k}, 1^1S; \mathbf{k_1}, 1^1S) \right) \right)
\end{aligned} \tag{6.42}$$

where

$$\mathbf{K} = \mathbf{k_1} - \mathbf{k_2} \qquad \mathbf{K_1} = \mathbf{k_1} - \mathbf{k} \qquad \mathbf{K_2} = \mathbf{k} - \mathbf{k_2}. \tag{6.43}$$

6.2.1 Evaluation of the Second Born Integrals

For atomic orbitals, expanded using a set of s type Slater functions ($\exp(-\alpha_i r)$), the first Born scattering amplitudes can be written in the general form (see eqn 6.11)

$$f^{(0)}(\mathbf{k_2}; \mathbf{k_1}) = \sum_{i=1}^{N} \left(\frac{1}{K^2} \frac{a_i b_i}{(K^2 + b_i^2)^2} \right) - \frac{1}{K^2} \tag{6.44}$$

which can be reduced using partial fractions to,

$$f^{(0)}(\mathbf{k_2}; \mathbf{k_1}) = \sum_{i=1}^{N} \left(\frac{a_i}{b_i^3} \frac{1}{K^2} - \frac{a_i}{b_i} \frac{1}{(K^2 + b_i^2)} - \frac{a_i}{b_i} \frac{1}{(K^2 + b_i^2)^2} \right) - \frac{1}{K^2}. \tag{6.45}$$

Now, for a correctly normalized orbital, $\sum a_i/b_i^3 = 1$ so the $1/K^2$ terms cancel and the first Born amplitudes from eqn 6.44 finally reduce to

$$f^{(0)}(\mathbf{k_2};\mathbf{k_1}) = \sum_{i=1}^{N}\left(-\frac{a_i}{b_i^3}\frac{1}{(K^2+b_i^2)} + \frac{a_i}{b_i}\frac{1}{(K^2+b_i^2)^2}\right). \tag{6.46}$$

This form of the first Born scattering amplitudes is useful, because when substituted into the closure approximation, eqn 6.42, all the resulting integrals are of the general form,

$$I_{lm} = \lim_{\eta\to 0^+}\int \frac{d\mathbf{k}}{(|\mathbf{k_1}-\mathbf{k}|^2+\mu_1^2)^l(|\mathbf{k}-\mathbf{k_2}|^2+\mu_2^2)^m(k^2-\bar{k}^2-i\eta)} \tag{6.47}$$

where $l, m = 1$ or 2. The l and/or $m = 2$ cases can be written in terms of the corresponding l and/or $m = 1$ integral by differentiation with respect to μ_1 or μ_2. For example,

$$\begin{aligned} I_{22} &= \lim_{\eta\to 0^+}\frac{1}{4\mu_1\mu_2}\frac{\partial^2}{\partial\mu_1\partial\mu_2}\left(\int\frac{d\mathbf{k}}{(K_1^2+\mu_1^2)(K_2^2+\mu_2^2)(k^2-\bar{k}^2-i\eta)}\right) \\ &= \frac{1}{4\mu_1\mu_2}\frac{\partial^2}{\partial\mu_1\partial\mu_2}(I_{11}). \end{aligned} \tag{6.48}$$

The solution of the general integral

$$I_{11}(\mathbf{k_1},\mu_1,\mathbf{k_2},\mu_2;\lambda) = \int\frac{d\mathbf{k}}{(|\mathbf{k_1}-\mathbf{k}|^2+\mu_1^2)(|\mathbf{k}-\mathbf{k_2}|^2+\mu_2^2)(k^2+\lambda^2)} \tag{6.49}$$

(where $i\lambda = \bar{k}$) has been determined by Lewis [91]. The related integral

$$I = \int\frac{d\mathbf{k}}{(|\mathbf{k_1}-\mathbf{k}|^2+\mu^2)(|\mathbf{k}-\mathbf{k_2}|^2+\mu^2)(k^2-\lambda^2+i\epsilon)} \tag{6.50}$$

has been given by Vachaspati [92] and Daltiz [93] (see appendix E).

For higher order s and p orbitals, the most general integral required for the calculation of the second Born matrix elements, after substitution of the first Born amplitudes, is

$$(I_{lm}, I_{lm,i}, I_{lm,ij}) = \int\frac{(1,k_i,k_ik_j)d\mathbf{k}}{(|\mathbf{k_1}-\mathbf{k}|^2+\mu_1^2)^l(|\mathbf{k_2}-\mathbf{k}|^2+\mu_2^2)^m(k^2+\lambda^2)} \tag{6.51}$$

where $i, j = x, y, z$. The denominator can be treated in the same manner as above. By

successive differentiation of the $l = m = 1$ case with respect to μ_1 and μ_2, the integrals $(I_{lm}, I_{lm,i}, I_{lm,ij})$ are obtained,

$$(I_{lm}, I_{lm,i}, I_{lm,ij}) = \frac{(-1)^{l+m}}{(l-1)!(m-1)!} \left(\frac{1}{2\mu_1}\right)^l \frac{\partial^l}{\partial \mu_1^l} \left(\frac{-1}{2\mu_2}\right)^m \frac{\partial^m}{\partial \mu_2^m} (I_{11}, I_{11,i}, I_{11,ij}) \tag{6.52}$$

Vachaspati [92] and Byron and Latour [68] give expressions for the $I_{11,i}$ terms and Dalitz [93] derives expressions for both the $I_{11,i}$ and $I_{11,ij}$ integrals.

As an example, the calculation of the $2p$ contribution to the ground state elastic scattering of electrons from atomic hydrogen is outlined. Using the exact hydrogen $1s$ and $2p$ target states, the first Born scattering amplitudes are

$$\begin{aligned} f^{(0)}(\mathbf{k_2}, 2p_m; \mathbf{k}_1, 1s) &= N \frac{1}{(K^2+\nu^2)^3} \frac{Y_{1m}(\hat{\mathbf{K}})}{K} \\ &= N \frac{1}{K^2(K_2+\nu^2)^3} K Y_{1m}(\hat{\mathbf{K}}) \\ &= N \left(\frac{1}{\nu^6}\frac{1}{K^2} - \frac{1}{\nu^6}\frac{1}{(K^2+\nu^2)} - \frac{1}{\nu^4}\frac{1}{(K^2+\nu^2)^2} \right. \\ &\quad \left. - \frac{1}{\nu^2}\frac{1}{(K^2+\nu^2)^3} \right) K Y_{1m}(\hat{\mathbf{K}}) \\ &= N K Y_{1m}(\hat{\mathbf{K}}) \sum_{i=1}^{4} \frac{a_i}{(K^2+b_i^2)^{n_i}}. \end{aligned} \tag{6.53}$$

Substituting into the second Born integral gives

$$I_m = N^2 \sum_{i=1}^{4}\sum_{j=1}^{4} \lim_{\eta \to 0^+} \int \frac{a_i K_1 Y_{1m}(\hat{\mathbf{K}}_1) a_j K_2 Y_{1m}^*(\hat{\mathbf{K}}_2) d\mathbf{k}}{(K_1^2+b_i^2)^{n_i}(K_2^2+b_j^2)^{n_j}(k^2-\bar{k}^2-i\eta)}. \tag{6.54}$$

The $2p$ contribution to the matrix element consists of the three terms I_1, I_2 and I_3 which when summed, can be written,

$$\begin{aligned} I_{2p} &= A \sum_{i=1}^{4}\sum_{j=1}^{4} \lim_{\eta \to 0^+} \int \frac{a_i a_j d\mathbf{k}}{(K_1^2+b_i^2)^{n_i}(K_2^2+b_j^2)^{n_j}(k^2-\bar{k}^2-i\eta)} \\ &\quad (K_{1x}K_{2x} + K_{1y}K_{2y} + K_{1z}K_{2z}) \end{aligned}$$

$$= A\sum_{i=1}^{4}\sum_{j=1}^{4}\lim_{\eta\to 0^+}\int \frac{a_i a_j d\mathbf{k}}{(K_1^2+b_i^2)^{n_i}(K_2^2+b_j^2)^{n_j}(k^2-\bar{k}^2-i\eta)} \left(\mathbf{k_1}\cdot\mathbf{k_2}+|\mathbf{k}|^2-\mathbf{k}\cdot(\mathbf{k_1}+\mathbf{k_2})\right). \quad (6.55)$$

Expression 6.55 is now simply the sum of terms of the form of $I_{lm}, I_{lm,i}$ and $I_{lm,ij}$, defined in eqn 6.51 The specific integrals can be calculated using the prescription of Dalitz, giving the $2p$ contribution to the second Born matrix element.

When Gaussian functions are used to expand the atomic orbitals, the expression for the first Born scattering amplitudes corresponding to eqn 6.44 is

$$f^{(0)}(\mathbf{k_2};\mathbf{k_1}) = \frac{1}{|\mathbf{k_1}-\mathbf{k_2}|^2}\left(\sum_{i=1}^{N} a_i e^{-b_i|\mathbf{k_1}-\mathbf{k_2}|^2} - 1\right). \quad (6.56)$$

Appendix G gives an account of the derivation of the corresponding second Born integrals. Because this is incomplete, another method of calculating the second Born integrals from functions of the form of eqn 6.56 was used. Fitting the elastic, first Born matrix elements calculated using eqn 6.56, to a non-linear function of the form

$$f^{(0)}(\mathbf{k_2};\mathbf{k_1}) \approx \sum_{i=1}^{M}\frac{a_i}{K^2+b_i^2} \quad (6.57)$$

leaves the required integrals of eqn 6.42 in the form of eqn 6.49. Substituting eqn 6.57 back into 6.42 leads to

$$\begin{aligned} f^{(1)}(\mathbf{k_2},0;\mathbf{k_1},0) &= \sum_{i=1}^{M}\sum_{j=1}^{M} a_i a_j \left[2I(\mathbf{k_1},b_i,\mathbf{k_2},b_j;-ik_0) - I(\mathbf{k_1},b_i,\mathbf{k_2},b_j;-i\bar{k})\right] \\ &\quad + \sum_{i=1}^{M} a_i \left[I(\mathbf{k_1},b_i,\mathbf{k_2},0;-i\bar{k}) + I(\mathbf{k_1},0,\mathbf{k_2},b_i;-i\bar{k})\right] \\ &\quad - I(\mathbf{k_1},0,\mathbf{k_2},0;-i\bar{k}) \end{aligned} \quad (6.58)$$

and using the result of Lewis, this expression can be evaluated analytically.

Higher order orbitals are fitted to functions of the form

$$f^{(0)}(\mathbf{k_2};\mathbf{k_1}) \approx \sum_{i=1}^{M} \frac{a_i}{(K^2+b_i^2)^{n_i}} \frac{Y_{LM}(\hat{\mathbf{K}})}{K^L} \tag{6.59}$$

which, when substituted, give expressions which can again be evaluated analytically.

6.2.2 Results

The second Born matrix elements were calculated in the closure approximation as described in section 6.2, using the first Born amplitudes calculated from the Byron and Joachain $1s$ helium orbital (see section 6.1).

The first Born amplitudes, calculated using the McKoy, 10 function Gaussian expansion of the helium $1s$ orbital, were fitted to a function of the form of eqn 6.57. This function was then used to calculate the second Born matrix elements through eqn 6.58. The procedure used to fit the first Born amplitudes is described in appendix H. It is known as the *Levenberg-Marquardt Method* and is a general, non-linear least squares fitting procedure. The figure of merit used is the χ^2, which is minimized with respect to the variable parameters used in the fitting function. 20 points were used in the fitting procedure, ranging from $K = 0$ to 95 in increments of $5a.u.$

Obviously, because the Gaussian and Slater first Born amplitudes are so close, fitting the Gaussian amplitudes using a function of the form of eqn 6.46 as a starting point, immediately gives a very close fit. Using this approach gives a χ^2 value of 0.1981×10^{-10}. The fitting function, denoted $(3,3)$, not surprisingly, is very similar to the original, eqn 6.46. The absolute value of the χ^2 term is dependent on the points chosen to be used in the fitting procedure and is of little practical value. It is only meaningful to use the χ^2 values as a comparison between various fitting functions. It was investigated whether a more simple fitting function could be found which adequately matched the Gaussian first Born amplitudes. The expansion

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = \sum_{i=1}^{M} \frac{a_i}{K^2+b_i^2}, \tag{6.60}$$

showed the lowest χ^2 value of 0.4017×10^{-9}, when $M = 2$. The same set of 20 points was used. Table 6.10 gives the first Born amplitudes from table 6.2 and the fitted amplitudes, from the $M = 2$ function.

The $M = 2$ expansion, which will be denoted the $(2,0)$ fit, is

$$f^{(0)}_{(2,0)}(K) = \frac{1.410}{K^2 + (4.789)^2} - \frac{5.418}{K^2 + (2.521)^2} \tag{6.61}$$

No improvement over the $(2,0)$ function could be obtained by including terms of the form

$$\frac{a}{(K^2 + b^2)^2}. \tag{6.62}$$

It can be seen from table 6.10, that the $(3,3)$ fitted functions are practically indistinguishable from the original amplitudes and the $(2,0)$ fitted amplitudes are also in excellent agreement. Because of it's relative simplicity, the $(2,0)$ function was used in the subsequent calculation of the second Born matrix elements.

Table 6.10: First Born scattering amplitudes calculated from the full expression for the $f^{(0)}(K)$, and from the $(2,0)$ fitted function

K	$f^{(0)}(K)$	$f^{(0)}(K)$ $(3,3)$ fit	$f^{(0)}(K)$ $(2,0)$ fit
0	-0.7910(0)	-0.7910(0)	-0.7910(0)
5	-0.1434(0)	-0.1434(0)	-0.1434(0)
10	-0.3949(-1)	-0.3949(-1)	-0.3947(-1)
15	-0.1773(-1)	-0.1773(-1)	-0.1773(-1)
20	-0.9992(-2)	-0.9991(-2)	-0.1000(-1)
25	-0.6398(-2)	-0.6398(-2)	-0.6406(-2)
30	-0.4444(-2)	-0.4444(-2)	-0.4450(-2)
35	-0.3266(-2)	-0.3265(-2)	-0.3270(-2)
40	-0.2500(-2)	-0.2500(-2)	-0.2504(-2)
45	-0.1976(-2)	-0.1976(-2)	-0.1979(-2)
50	-0.1600(-2)	-0.1600(-2)	-0.1603(-2)
55	-0.1323(-2)	-0.1323(-2)	-0.1325(-2)
60	-0.1111(-2)	-0.1111(-2)	-0.1113(-2)
65	-0.9469(-3)	-0.9469(-3)	-0.9486(-2)
70	-0.8165(-3)	-0.8165(-3)	-0.8179(-3)
75	-0.7112(-3)	-0.7112(-3)	-0.7125(-3)
80	-0.6252(-3)	-0.6251(-3)	-0.6262(-3)
85	-0.5537(-3)	-0.5537(-3)	-0.5547(-3)
90	-0.4939(-3)	-0.4939(-3)	-0.4948(-3)
95	-0.4433(-3)	-0.4433(-3)	-0.4441(-3)
100	-0.4001(-3)		

The helium, second Born matrix elements calculated from the Byron and Joachain, Slater $1s$ orbital at 200, 300, 400 and $500eV$ are given in table 6.11. Also given are the results of using the $(2,0)$ fit to the 10 function Gaussian, first Born amplitudes. The $300eV$ Gaussian

results are compared with the quoted values of Byron and Joachain in table 6.12. The closure energy used is the value given by Byron and Joachain of $\Delta = 1.3a.u.$ Thus $\bar{k}^2 = k_0^2 - 2.6$ where k_0 is the incident energy. The value of the closure energy was chosen so that the imaginary part of the forward scattering amplitude, matches the total cross section calculated using the Bethe-Born approximation at $500eV$ calculated by Inokuti *et al.* [94] as required by the optical theorem (see section 5.3.1).

Table 6.11: Second Born scattering amplitudes, calculated analytically, and from the $(2,0)$ fitted function

	$200eV$	
Scattering angle	Slater	Gaussian
5	0.4338(0), 0.7969(0) [3]	0.4333(0), 0.7959(0)
10	0.2467(0), 0.6281(0)	0.2465(0), 0.6274(0)
15	0.1546(0), 0.4789(0)	0.1545(0), 0.4784(0)
20	0.1112(0), 0.3728(0)	0.1112(0), 0.3725(0)
25	0.8974(-1), 0.3024(0)	0.8971(-1), 0.3021(0)
30	0.7786(-1), 0.2565(0)	0.7781(-1), 0.2562(0)
	$300eV$	
5	0.2589(0), 0.6605(0)	0.2586(0), 0.6597(0)
10	0.1237(0), 0.4627(0)	0.1236(0), 0.4622(0)
15	0.7766(-1), 0.3319(0)	0.7764(-1), 0.3316(0)
20	0.5999(-1), 0.2548(0)	0.5998(-1), 0.2545(0)
25	0.5142(-1), 0.2095(0)	0.5139(-1), 0.2093(0)
30	0.4579(-1), 0.1818(0)	0.4575(-1), 0.1815(0)
	$400eV$	
5	0.1676(0), 0.5562(0)	0.1674(0), 0.5555(0)
10	0.7459(-1), 0.3604(0)	0.7456(-1), 0.3601(0)
15	0.4972(-1), 0.2527(0)	0.4971(-1), 0.2526(0)
20	0.4060(-1), 0.1956(0)	0.4058(-1), 0.1954(0)
25	0.3542(-1), 0.1637(0)	0.3539(-1), 0.1635(0)
30	0.3130(-1), 0.1441(0)	0.3127(-1), 0.1438(0)
	$500eV$	
5	0.1154(0), 0.4766(0)	0.1153(0), 0.4761(0)
10	0.5106(-1), 0.2938(0)	0.5105(-1), 0.2935(0)
15	0.3623(-1), 0.2048(0)	0.3623(-1), 0.2046(0)
20	0.3042(-1), 0.1605(0)	0.3041(-1), 0.1603(0)
25	0.2645(-1), 0.1361(0)	0.2643(-1), 0.1359(0)
30	0.2298(-1), 0.1205(0)	0.2295(-1), 0.1203(0)

Table 6.14 gives the second Born amplitudes at $300eV$ for the three different expansions of

[3] Elements in tables written a, b represent the complex number $a + ib$

Table 6.12: Second Born amplitudes from Byron and Joachain, and calculated from the Gaussian, $(0,2)$ fit

Scattering angle	Byron and Joachain	Gaussian
5	0.259(0), 0.661(0)	0.2586(0), 0.6597(0)
10	0.124(0), 0.463(0)	0.1236(0), 0.4622(0)
15	0.78(-1), 0.332(0)	0.7764(-1), 0.3316(0)
20	0.60(-1), 0.255(0)	0.5998(-1), 0.2545(0)
25	0.52(-1), 0.210(0)	0.5139(-1), 0.2093(0)
30	0.46(-1), 0.182(0)	0.4575(-1), 0.1815(0)

Table 6.13: χ^2 values for the first Born amplitudes, calculated for the 20 points $K = 0 - 95 a.u.$

Slater/Slater fit	Gauss(10)/Gauss(10) fit	Gauss(5)/Gauss(5) fit
0.3447(-9)	0.4017(-9)	0.1606(-10)
Slater/Gauss(10)	Slater/Gauss(5)	
0.2639(-6)	0.5151(-4)	

the helium $1s$ orbital (see section 6.1). The second Born amplitudes are calculated via $(2,0)$ fitting functions. Also given is the Slater exact results from table 6.11. Table 6.13 gives the χ^2 values for these fits. Also given is the χ^2 values for the exact Slater and Gaussian amplitudes from table 6.2 compared with each other, calculated from the same 20 points as the fitted functions. From table 6.13, it can be seen that the $(2,0)$ fitted functions match the exact amplitudes significantly better that the exact amplitudes match each other. Comparing the exact Slater, and the $(2,0)$ fitted Slater results from table 6.14 gives a measure of the error introduced in using a fitted function rather than the exact amplitudes in the calculation of the second Born matrix elements. Interestingly, the Gaussian(10) results are very close to the $(2,0)$ Slater second Born matrix elements. This is not necessarily what would be expected when considering the various χ^2 values, and is considered a fortuitous accident rather than having any underlying significance, with respect to the two methods of calculation. The results as a whole, compare very well and do not seem too sensitive to the detail of the first Born amplitudes or the fitting procedure.

6.2.3 Inclusion of Intermediate States

Eqn 6.35 can be extended to include intermediate states beyond the ground state. The next two lowest lying singlet states for helium, are the 2^1S and 2^1P states. Writing the first Born

Table 6.14: $300eV$ second Born scattering amplitudes calculated from the two function fit to the first Born amplitudes evaluated using the two function Slater $1s$ orbital of Byron and Joachain and the 5 and 10 function Gaussian orbitals of McKoy *et al.*

Scattering Angle	Slater exact	Slater fitted
5	0.2589(0), 0.6605(0)	0.2587(0), 0.6599(0)
10	0.1237(0), 0.4627(0)	0.1236(0), 0.4622(0)
15	0.7766(-1), 0.3319(0)	0.7764(-1), 0.3316(0)
20	0.5999(-1), 0.2548(0)	0.5998(-1), 0.2546(0)
25	0.5142(-1), 0.2095(0)	0.5139(-1), 0.2093(0)
30	0.4579(-1), 0.1818(0)	0.4575(-1), 0.1816(0)
	Gaussian $10s$ basis	Gaussian $5s$ basis
5	0.2586(0), 0.6597(0)	0.2572(0),0.6556(0)
10	0.1236(0), 0.4622(0)	0.1232(0),0.4597(0)
15	0.7764(-1), 0.3316(0)	0.7756(-1),0.3300(0)
20	0.5998(-1), 0.2545(0)	0.5998(-1),0.2533(0)
25	0.5139(-1), 0.2093(0)	0.5140(-1),0.2083(0)
30	0.4575(-1), 0.1815(0)	0.4577(-1),0.1806(0)

amplitudes for the elastic, $2^1S \rightarrow 1^1S$ and $2^1P \rightarrow 1^1S$ as

$$f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = N_{1^1S}^2 \frac{1}{K^2} \langle \phi_{1s}^{\mathrm{He}} | e^{i\mathbf{K}\cdot\mathbf{r}} - 1 | \phi_{1s}^{\mathrm{He}} \rangle \tag{6.63}$$

$$f^{(0)}(\mathbf{k_2}, 2^1S; \mathbf{k_1}, 1^1S) = N_{1^1S} N_{2^1S} \frac{1}{K_2} \langle \phi_{2s}^{\mathrm{He}} | e^{i\mathbf{K}\cdot\mathbf{r}} - 1 | \phi_{1s}^{\mathrm{He}} \rangle \tag{6.64}$$

$$f^{(0)}(\mathbf{k_2}, 2^1P_m; \mathbf{k_1}, 1^1S) = N_{1^1S} N_{2^1P} \frac{1}{K^2} \langle \phi_{2p_m}^{\mathrm{He}} | e^{i\mathbf{K}\cdot\mathbf{r}} - 1 | \phi_{1s}^{\mathrm{He}} \rangle \tag{6.65}$$

respectively, the closure approximation to the second Born, elastic matrix elements including these states is

$$\begin{aligned} f^{(1)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) = & \\ & I_b(1^1S; k_{1^1S}) + I_b(2^1S; k_{2^1S}) + \sum_{m=1}^{3} I_b(2^1P_m; k_{2^1P}) \\ & - I_b(1^1S; \bar{k}) - I_b(2^1S; \bar{k}) - \sum_{m=1}^{3} I_b(2^1P_m; \bar{k}) \end{aligned}$$

$$+I_c(\bar{k}) \tag{6.66}$$

where $I_b(n,z)$ and $I_c(\bar{k})$ have been defined in eqns 6.36 and 6.38 respectively. Writing the Byron and Joachain expression for the second Born matrix elements, eqn 6.42, as $f_C^{(1)}(1^1S;\bar{k})$, eqn 6.66 can be written

$$\begin{aligned} f^{(1)}(\mathbf{k_2},1^1S;\mathbf{k_1},1^1S) &= f_C^{(1)}(1^1S,\bar{k}) + I_b(2^1S,k_{2^1S}) - I_b(2^1S,\bar{k}) \\ &\quad + \sum_{m=1}^{3}\left(I_b(2^1P_m,k_{2^1P}) - I_b(2^1P_m;\bar{k})\right). \end{aligned} \tag{6.67}$$

Thus, the only additional terms required for the calculation of the second Born amplitudes via eqn 6.66, are the I_b terms for the 2^1S and 2^1P states.

2^1S Contribution

Using the helium $1s$ and $2s$ orbitals from eqns 6.10 and 6.27 respectively, the first Born inelastic scattering amplitudes from eqn 6.29, can be written in the form

$$\begin{aligned} f^{(0)}(\mathbf{k_2},2^1S;\mathbf{k_1},1^1S) &= \frac{A}{K^2(K^2+a^2)^2} + \frac{B}{K^2(K^2+b^2)^2} \\ &\quad + \frac{C(3c^2-K^2)}{K^2(K^2+c^2)^3} + \frac{D(3d^2-K^2)}{K^2(K^2+d^2)^3} \end{aligned} \tag{6.68}$$

Using the ideas introduced in section 6.2.1, this expression can be reduced to one of the form

$$f^{(0)}(\mathbf{k_2},2^1S;\mathbf{k_1},1^1S) = \sum_i \frac{\alpha_i}{(K^2+\beta_i^2)^{n_i}}, \tag{6.69}$$

which, when substituted into the expression for the integral I_b, can be written as the sum of the integrals $I_{11}(\mathbf{k_1},\beta_i,\mathbf{k_2},\beta_j;\bar{k})$ and it's derivatives with respect to β_i and β_j. The calculation of I_b requires the calculation of terms I_{31}, I_{32} and I_{33}. These were calculated by numerically differentiating the corresponding lower order term, rather than attempting to determine the

explicit expression, which is a very complicated function.

The contributions from the 2^1S state to the elastic second Born amplitudes, are given in tables 6.15. The first column gives the I_b term calculated using the 2^1S intermediate energy of $0.75775a.u.$ which is the accurate value of Weiss, quoted by Kim and Inokuti [86]. The final two columns give the contribution calculated at the closure energy of Holt *et al.* [71] and Buckley and Walters [72] respectively.

The inelastic Slater first Born amplitudes were also fitted using eqn 6.57 allowing the calculation of the I_b terms from a simplified function. The integrals $I_b(2^1S, k_{2^1S})$ and $I_b(2^1S, \bar{k})$ from eqn 6.66 again reduce to the integrals defined in eqn 6.49.

The first Born amplitudes from table 6.7 were fitted from $K = 0$ to ∞. The threshold for excitation of the 2^1S state, from the calculations of Weiss, is $0.75775a.u.$ The non-physical region below threshold was included because the integral over $\mathbf{k}$ in eqn 6.36 runs over all $\mathbf{k}$ space, and thus, includes the off shell components of the first Born amplitudes.

The 2^1S first Born amplitudes were again fitted using the Levenberg-Marquardt method. Because of the rapid fall off of the first Born matrix elements, the range of fitting was reduced to $0 \longrightarrow 10a.u.$ using 20 points. Above $10a.u.$ the first Born matrix elements become very small and thus it is questionable whether it is useful to attempt to fit to these values. The best fit was obtained from the two term function

$$f^{(0)}_{fit2}(K) = \frac{1.795}{(K^2 + (1.670)^2)^2} - \frac{1.969}{(K^2 + (4.236)^2)^2}, \tag{6.70}$$

which gives a χ^2 value for the 20 points ranging from $K = 0 \longrightarrow 9.5a.u.$ in increments of $0.5a.u.$, of 0.2761×10^{-4} which was considered reasonable. Table 6.16 gives the $2^1S \leftarrow 1^1S$ first Born amplitudes calculated from the wave functions described by Holt *et al.* and from eqn 6.70. Figure 6-4 graphs the fitted and exact first Born $2^1S \rightarrow 1^1S$ amplitudes.

Table 6.17 gives the $300eV$ results from table 6.15 and the same terms calculated from the fitted first Born amplitudes for comparison. Also given are the I_b terms, calculated from the Hartree-Fock first Born amplitudes, evaluated using the McKoy Gaussian basis, and fitted to a two term function similar to eqn 6.70.

Comparison of the Slater results from table 6.17 show the simple fitted function does not reproduce the first Born amplitudes with sufficient accuracy required for the subsequent eval-

Table 6.15: 2^1S I_b terms calculated at the intermediate energy of Weiss and at the closure energies of Holt *et al.* and Buckley and Walters

Scattering Angle	$\epsilon_{2^1S} = 0.75775$	$\Delta = 0.84245$	$\Delta = 1.45$
		$200eV$	
5	0.3504(-3), 0.1148(-2)	0.3779(-3), 0.1137(-2)	0.5589(-3), 0.1029(-2)
10	0.3191(-3), 0.1083(-2)	0.3450(-3), 0.1074(-2)	0.5170(-3), 0.9760(-3)
15	0.2733(-3), 0.9854(-3)	0.2969(-3), 0.9775(-3)	0.4539(-3), 0.8941(-3)
20	0.2204(-3), 0.8668(-3)	0.2410(-3), 0.8607(-3)	0.3800(-3), 0.7938(-3)
25	0.1675(-3), 0.7400(-3)	0.1850(-3), 0.7357(-3)	0.3044(-3), 0.6853(-3)
30	0.1199(-3), 0.6159(-3)	0.1343(-3), 0.6132(-3)	0.2340(-3), 0.5776(-3)
		$300eV$	
5	0.2289(-3), 0.9396(-3)	0.2472(-3), 0.9340(-3)	0.3714(-3), 0.8768(-3)
10	0.1984(-3), 0.8592(-3)	0.2150(-3), 0.8545(-3)	0.3287(-3), 0.8052(-3)
15	0.1565(-3), 0.7436(-3)	0.1708(-3), 0.7400(-3)	0.2691(-3), 0.7014(-3)
20	0.1126(-3), 0.6129(-3)	0.1242(-3), 0.6105(-3)	0.2051(-3), 0.5832(-3)
25	0.7380(-4), 0.4851(-3)	0.8284(-4), 0.4838(-3)	0.1465(-3), 0.4662(-3)
30	0.4358(-4), 0.3720(-3)	0.5038(-4), 0.3715(-3)	0.9866(-4), 0.3614(-3)
		$400eV$	
5	0.1685(-3), 0.8103(-3)	0.1822(-3), 0.8067(-3)	0.2760(-3), 0.7704(-3)
10	0.1390(-3), 0.7183(-3)	0.1510(-3), 0.7155(-3)	0.2339(-3), 0.6857(-3)
15	0.1010(-3), 0.5922(-3)	0.1108(-3), 0.5903(-3)	0.1788(-3), 0.5690(-3)
20	0.6480(-4), 0.4593(-3)	0.7222(-4), 0.4582(-3)	0.1244(-3), 0.4448(-3)
25	0.3632(-4), 0.3395(-3)	0.4167(-4), 0.3391(-3)	0.7965(-4), 0.3318(-3)
30	0.1702(-4), 0.2426(-3)	0.2073(-4), 0.2426(-3)	0.4728(-4), 0.2393(-3)
		$500eV$	
5	0.1325(-3), 0.7198(-3)	0.1433(-3), 0.7173(-3)	0.2183(-3), 0.6918(-3)
10	0.1040(-3), 0.6188(-3)	0.1131(-3), 0.6169(-3)	0.1773(-3), 0.5971(-3)
15	0.6965(-4), 0.4868(-3)	0.7674(-4), 0.4857(-3)	0.1266(-3), 0.4727(-3)
20	0.3973(-4), 0.3565(-3)	0.4479(-4), 0.3560(-3)	0.8069(-4), 0.3488(-3)
25	0.1873(-4), 0.2478(-3)	0.2214(-4), 0.2477(-3)	0.4648(-4), 0.2444(-3)
30	0.6284(-5), 0.1665(-3)	0.8484(-5), 0.1666(-3)	0.2436(-4), 0.1656(-3)

Table 6.16: $2^1S \leftarrow 1^1S$ first Born amplitudes calculated from the Helium states of Holt *et al.* and from the $2^1S \leftarrow 1^1S$ fitted function

K	$f^{(0)}_{2^1S\leftarrow 1^1S}$ (Holt *et al.*)	$f^{(0)}_{2^1S\leftarrow 1^1S}$ (fitted)
0.0	0.2248(0)	0.2250(0)
0.5	0.1885(0)	0.1885(0)
1.0	0.1196(0)	0.1181(0)
1.5	0.6589(-1)	0.6316(-1)
2.0	0.3487(-1)	0.3203(-1)
2.5	0.1861(-1)	0.1633(-1)
3.0	0.1021(-1)	0.8583(-2)
3.5	0.5778(-2)	0.4688(-2)
4.0	0.3376(-2)	0.2663(-2)
4.5	0.2032(-2)	0.1570(-2)
5.0	0.1257(-2)	0.9577(-3)
5.5	0.7968(-3)	0.6027(-3)
6.0	0.5164(-3)	0.3901(-3)
6.5	0.3415(-3)	0.2590(-3)
7.0	0.2299(-3)	0.1760(-3)
7.5	0.1573(-3)	0.1221(-3)
8.0	0.1092(-3)	0.8632(-4)
8.5	0.7675(-4)	0.6209(-4)
9.0	0.5456(-4)	0.4538(-4)
9.5	0.3916(-4)	0.3364(-4)

Table 6.17: I_b terms calculated analytically, and using the $2^1S \leftarrow 1^1S$ fitted function, for an incident energy of $300eV$, and $\Delta = 0.75775a.u.$

Scattering Angle	Analytic	Fitted (Slater)	Fitted (Gaussian)
5	0.2289(-3), 0.9396(-3)	0.3250(-3), 0.1698(-2)	0.2527(-3), 0.1352(-2)
10	0.1984(-3), 0.8592(-3)	0.2465(-3), 0.1423(-2)	0.1936(-3), 0.1143(-2)
15	0.1565(-3), 0.7436(-3)	0.1585(-3), 0.1085(-2)	0.1250(-3), 0.8792(-3)
20	0.1126(-3), 0.6129(-3)	0.8742(-4), 0.7724(-3)	0.6763(-4), 0.6270(-3)
25	0.7380(-4), 0.4851(-3)	0.4060(-4), 0.5262(-3)	0.2878(-4), 0.4224(-3)
30	0.4358(-4), 0.3720(-3)	0.1395(-4), 0.3498(-3)	0.6562(-5), 0.2730(-3)

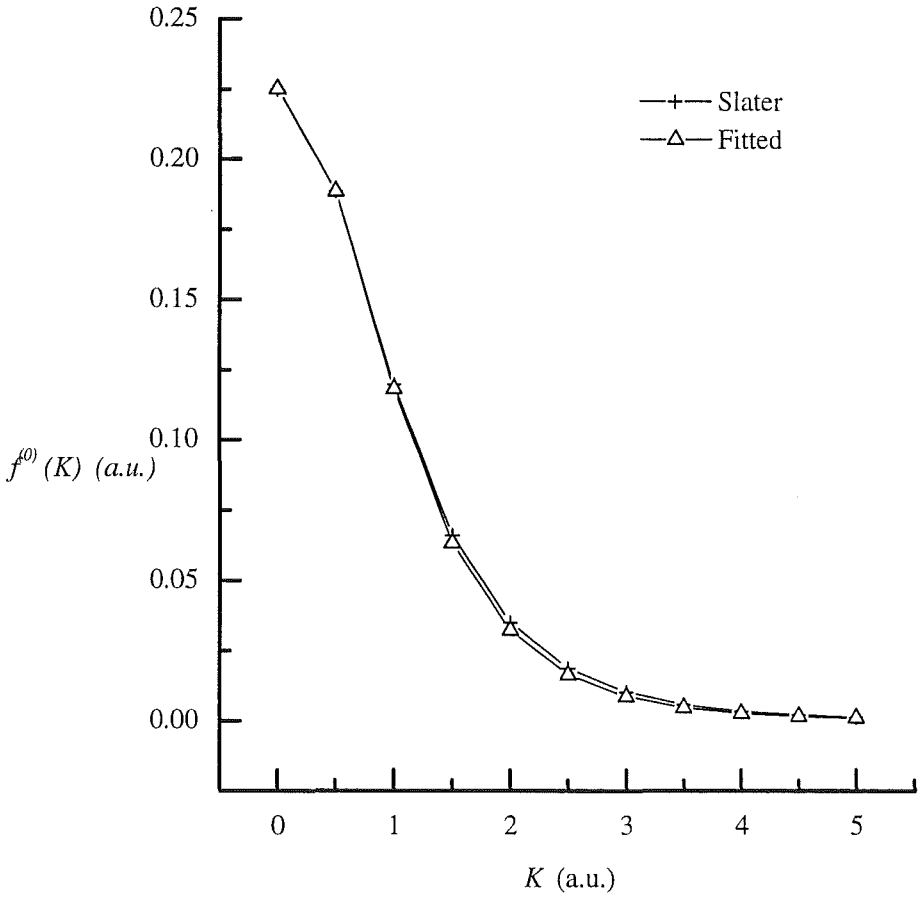


Figure 6-4: Analytic and fitted helium $2^1S \leftarrow 1^1S$ generalised oscillator strengths

uation of the second Born, I_b terms. It is anticipated that the first Born amplitudes could be fitted to greater accuracy by more extensive functions than the simple two term expression 6.70. The problem with this is the Levenberg-Marquardt method only determines the local minima of the figure of merit from the defined initial point. Using fitting functions with more variables means the resulting optimisation contains a larger number of local minima thus making it more difficult to systematically search for the global minima. Other approaches to the optimisation must be used in this case.

2^1P Contribution

The calculation of the 2^1P contribution to the second Born matrix elements, proceeds in the same manner as the $2p$ case for atomic hydrogen scattering, outlined in section 6.2.1. The first Born scattering amplitudes, from section 6.1.2 are

$$f^{(0)}(\mathbf{k_2}, 2^1P; \mathbf{k_1} 1^1S) = \sum_{m=1}^{3} f^{(0)}(\mathbf{k_2}, 2^1P_m; \mathbf{k_1}, 1^1S). \tag{6.71}$$

Using the 2^1P wave function of Holt *et al.*, eqn 6.32, the individual scattering amplitudes, $f^{(0)}(\mathbf{k_2}, 2^1P_m; \mathbf{k_1}, 1^1S)$ can be written

$$f^{(0)}(\mathbf{k_2}, 2^1P_m; \mathbf{k_1}, 1^1S) = N_{2^1P} \sum_{i=1}^{2} \left(\frac{A_i}{K^2(K^2+\lambda_i^2)^3} \right) K Y_{1m}(\hat{\mathbf{K}}). \tag{6.72}$$

Substituting this into the equation for the second Born matrix elements, eqn 6.66, gives the expression for the 2^1P contribution to $f^{(1)}(\mathbf{k_2}, 1^1S; \mathbf{k_1} 1^1S)$,

$$f^{(1)}_{2^1P} = N^2_{2^1P} \sum_{m=1}^{3} \sum_{i=1}^{2} \sum_{j=1}^{2} \left(A_i A_j \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{K_1 Y^*_{1m}(\hat{\mathbf{K}}_1) K_2 Y_{1m}(\hat{\mathbf{K}}_2)}{K_1^2(K_1^2+\lambda_i^2)^3 K_2^2(K_2^2+\lambda_j^2)^3 (k^2 - \bar{k}^2 - i\eta)} \right) \tag{6.73}$$

The numerator three terms associated with the magnetic substates $m = 0, \pm 1$, can be combined (see eqn 6.55),

$$\sum_{m=1}^{3}\left(K_1 Y_{1m}^{*}(\hat{\mathbf{K}}_1) K_2 Y_{1m}(\hat{\mathbf{K}}_2)\right) =$$
$$\frac{3}{4\pi}\left(K_{1x}K_{2x} + K_{1y}K_{2y} + K_{1z}K_{2z}\right)$$
$$= \mathbf{k_1}\cdot\mathbf{k_2} - (\mathbf{k_1}+\mathbf{k_2})\cdot\mathbf{k} + \mathbf{k}\cdot\mathbf{k}, \tag{6.74}$$

and the denominator can be reduced using partial fractions, (see eqn 6.53),

$$\frac{1}{K_2(K_2+\lambda^2)^3} = \frac{1}{\lambda^6}\frac{1}{K^2} - \frac{1}{\lambda^6}\frac{1}{(K^2+\lambda^2)} - \frac{1}{\lambda^4}\frac{1}{(K^2+\lambda^2)^2} - \frac{1}{\lambda^2}\frac{1}{(K^2+\lambda^2)^3}$$
$$= \sum_{k=1}^{4}\frac{a_k}{(K^2+b_k)^{n_k}}. \tag{6.75}$$

Substituting into eqn 6.73 gives,

$$f_{2^1P}^{(1)} = \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{4}\sum_{l=1}^{4}(\mathbf{k_1}\cdot\mathbf{k_2} I_{n_k n_l} - (k_{1x}+k_{2x})I_{n_k n_l,x} - (k_{1y}+k_{2y})I_{n_k n_l,y}$$
$$-(k_{1z}+k_{2z})I_{n_k n_l,z} + I_{n_k n_l,xx} + I_{n_k n_l,yy} + I_{n_k n_l,zz})_{\mu_1=\lambda_i,\,\mu_2=\lambda_j}. \tag{6.76}$$

The integrals $I_{n_k n_l}, I_{n_k n_l,x}$ and $I_{n_k n_l,xx}$ etc. are defined in eqn 6.51, and are related to the corresponding $I_{11}, I_{11,x}$ and $I_{11,xx}$ etc. terms through differentiation with respect to the parameters μ_1 and μ_2.

Calculation of the integrals $I_{11,m}$ and $I_{11,mm}$ was completed using equations (A4) and (A6) from the paper by Dalitz [93]. The integral over Z was completed using 128 point Gauss-Legendre quadrature. The differentiations required for the evaluation of higher order terms were completed numerically.

Table 6.18 gives the 2^1P second Born matrix elements, from the Holt *et al.* wave function, calculated using the 2^1P energy of $0.77988 a.u.$ and the closure energies of $0.84245 a.u.$ and $1.45 a.u.$ The numerical results are somewhat larger than the 2^1S terms, and have a more

Table 6.18: 2^1P I_b terms calculated at the intermediate energy of Weiss and at the closure energies of Holt *et al.* and Buckley and Walters

Scattering Angle	$\epsilon_{2^1P} = 0.77988$	$\Delta = 0.84245$	$\Delta = 1.45$
		$200eV$	
5	-0.3214(0), -0.6680(-1)	-0.3005(0), -0.5646(-1)	-0.1866(0), -0.2472(-1)
10	0.1792(-1), -0.1180(-1)	0.1441(-1), -0.1379(-1)	-0.1028(-1), -0.1891(-1)
15	0.3913(-1), -0.1294(-2)	0.3493(-1), -0.4399(-2)	0.4665(-2), -0.1411(-1)
20	0.1895(-1), -0.2617(-2)	0.1640(-1), -0.4524(-2)	-0.2497(-2), -0.9896(-2)
25	0.3560(-2), -0.3382(-2)	0.2302(-2), -0.4216(-2)	-0.7044(-2), -0.5733(-2)
30	-0.3073(-2), -0.1832(-2)	-0.3542(-2), -0.2052(-2)	-0.6995(-2), -0.1703(-2)
		$300eV$	
5	-0.2639(0), -0.1014(0)	-0.2506(0), -0.8919(-1)	-0.1611(0), -0.4519(-1)
10	0.1101(0), 0.2170(-1)	0.1036(0), 0.1412(-1)	0.5245(-1), -0.2448(-1)
15	0.7258(-1), 0.1461(-1)	0.6842(-1), 0.9161(-2)	0.3331(-1), -0.1889(-1)
20	0.2368(-1), -0.9148(-3)	0.2185(-1), -0.3187(-2)	0.5967(-2), -0.1442(-1)
25	0.1112(-2), -0.4831(-2)	0.5390(-3), -0.5380(-2)	-0.4549(-2), -0.7625(-2)
30	-0.5712(-2), -0.1806(-2)	-0.5678(-2), -0.1635(-2)	-0.5445(-2), -0.4494(-3)
		$400eV$	
5	-0.1457(0), -0.9137(-1)	-0.1408(0), -0.8397(-1)	-0.9849(-1), -0.5438(-1)
10	0.1688(0), 0.5809(-1)	0.1618(0), 0.4684(-1)	0.1020(0), -0.1751(-1)
15	0.7561(-1), 0.1976(-1)	0.7230(-1), 0.1412(-1)	0.4240(-1), -0.1848(-1)
20	0.1520(-1), -0.4362(-2)	0.1411(-1), -0.5954(-2)	0.4039(-2), -0.1480(-1)
25	-0.5041(-2), -0.5977(-2)	-0.5149(-2), -0.5925(-2)	-0.6211(-2), -0.5344(-2)
30	-0.9229(-2), -0.3617(-3)	-0.8932(-2), 0.2100(-3)	-0.6238(-2), 0.3510(-2)
		$500eV$	
5	-0.1719(-1), -0.4952(-1)	-0.1846(-1), -0.4917(-1)	-0.1964(-1), -0.5160(-1)
10	0.1994(0), 0.8516(-1)	0.1927(0), 0.7208(-1)	0.1334(0), -0.7338(-2)
15	0.6593(-1), 0.1679(-1)	0.6345(-1), 0.1185(-1)	0.4013(-1), -0.1831(-1)
20	0.5254(-2), -0.8412(-2)	0.4679(-2), -0.9203(-2)	-0.7876(-3), -0.1378(-1)
25	-0.1010(-1), -0.5768(-2)	-0.9939(-2), -0.9939(-2)	-0.8454(-2), -0.1881(-2)
30	-0.1191(-1), 0.1331(-2)	-0.1150(-1), 0.2161(-2)	-0.7619(-2), 0.7093(-2)

complicated angular dependence. As with the 2^1S results, the integrals are not strong functions of Δ, with the dependence being strongest at small angles and low energies.

The Closure Term

The expression for the second Born amplitude, using the closure approximation and including the $1^1S, 2^1S$ and 2^1P helium states is given by eqn 6.67. The $f_C^{(1)}(1^1S, \bar{k})$ term is, from eqn 6.42,

$$
\begin{aligned}
f_C^{(1)}(1^1S, \bar{k}) = & \\
& \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi^{\mathrm{He}}_{1^1S} | V | \phi_{\mathbf{k}} \psi^{\mathrm{He}}_{1^1S} \rangle \langle \phi_{\mathbf{k}} \psi^{\mathrm{He}}_{1^1S} | V | \phi_{\mathbf{k_1}} \psi^{\mathrm{He}}_{1^1S} \rangle}{k^2 - k_0^2 - i\eta} \\
& - \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k_2}} \psi^{\mathrm{He}}_{1^1S} | V | \phi_{\mathbf{k}} \psi^{\mathrm{He}}_{1^1S} \rangle \langle \phi_{\mathbf{k}} \psi^{\mathrm{He}}_{1^1S} | V | \phi_{\mathbf{k_1}} \psi^{\mathrm{He}}_{1^1S} \rangle}{k^2 - \bar{k}^2 - i\eta} \\
& + \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \psi^{\mathrm{He}}_{1^1S} | \langle \phi_{\mathbf{k_2}} | V | \phi_{\mathbf{k}} \rangle \langle \phi_{\mathbf{k}} | V | \phi_{\mathbf{k_1}} \rangle | \psi^{\mathrm{He}}_{1^1S} \rangle}{k^2 - \bar{k}^2 - i\eta} \\
= \; & 16\pi^2 \left(\lim_{\eta \to 0^+} \int \frac{4d\mathbf{k}}{(k^2 - k_0^2 - i\eta)} f^{(0)}(\mathbf{k}2, 1^1S; \mathbf{k}, 1^1S) f^{(0)}(\mathbf{k}, 1^1S; \mathbf{k_1}, 1^1S) \right. \\
& - \lim_{\eta \to 0^+} \int \frac{2d\mathbf{k}}{(k^2 - \bar{k}^2 - i\eta)} f^{(0)}(\mathbf{k}2, 1^1S; \mathbf{k}, 1^1S) f^{(0)}(\mathbf{k}, 1^1S; \mathbf{k_1}, 1^1S) \\
& + \lim_{\eta \to 0^+} \int \frac{2d\mathbf{k}}{(k^2 - \bar{k}^2 - i\eta)} \left(\frac{K^2}{K_1^2 K_2^2} f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k_1}, 1^1S) \right. \\
& \left. \left. - \frac{1}{K_1^2} f^{(0)}(\mathbf{k_2}, 1^1S; \mathbf{k}, 1^1S) - \frac{1}{K_2^2} f^{(0)}(\mathbf{k}, 1^1S; \mathbf{k_1}, 1^1S) \right) \right)
\end{aligned}
\tag{6.77}
$$

This expression was evaluated from the first Born scattering amplitudes, calculated from the two term Slater $1s$ helium orbital of Byron and Joachain as described in section 6.2.2. Table 6.19 gives the closure integrals calculated using the Holt *et al.* and the Buckley and Walters closure energies in the energy range $200eV$ to $500eV$. Not surprisingly, the results for $\Delta = 1.45$ are very similar to the Byron and Joachain results of table 6.11 who used the same expression , with $\Delta = 1.35$. The Holt *at al.* results with $\Delta = 0.84245$ are in reasonably good agreement indicating that the $f_C^{(1)}$ terms are relatively insensitive to Δ. This is encouraging as Δ is a free parameter in the closure approximation, so for this approximation to be considered a reliable method, it should not be a strong function of Δ.

Table 6.20 gives the full second Born amplitudes calculated with the 2^1S and 2^1P interme-

Table 6.19: $f_C^{(1)}(1^1S, \bar{k})$ terms calculated using the Byron and Joachain $1s$ helium orbital for the elastic first Born amplitudes, and the two closure energies of Holt *et al.* and Buckley and Walters

	$200eV$	
Scattering Angle	$\Delta = 0.84245$	$\Delta = 1.45$
5	0.3512(0), 0.8887(0)	0.4504(0), 0.7665(0)
10	0.1859(0), 0.6391(0)	0.2647(0), 0.6188(0)
15	0.1273(0), 0.4680(0)	0.1654(0), 0.4794(0)
20	0.1027(0), 0.3606(0)	0.1161(0), 0.3758(0)
25	0.8970(-1), 0.2936(0)	0.9132(-1), 0.3053(0)
30	0.8098(-1), 0.2510(0)	0.7786(-1), 0.2586(0)
	$300eV$	
5	0.1919(0), 0.6947(0)	0.2759(0), 0.6453(0)
10	0.9748(-1), 0.4545(0)	0.1335(0), 0.4628(0)
15	0.7194(-1), 0.3224(0)	0.8102(-1), 0.3344(0)
20	0.6113(-1), 0.2489(0)	0.6055(-1), 0.2568(0)
25	0.5420(-1), 0.2066(0)	0.5102(-1), 0.2108(0)
30	0.4846(-1), 0.1805(0)	0.4519(-1), 0.1825(0)
	$400eV$	
5	0.1198(0), 0.5653(0)	0.1817(0), 0.5493(0)
10	0.6349(-1), 0.3515(0)	0.7957(-1), 0.3624(0)
15	0.4961(-1), 0.2471(0)	0.5059(-1), 0.2547(0)
20	0.4281(-1), 0.1929(0)	0.4029(-1), 0.1967(0)
25	0.3757(-1), 0.1627(0)	0.3492(-1), 0.1642(0)
30	0.3290(-1), 0.1438(0)	0.3087(-1), 0.1443(0)
	$500eV$	
5	0.8250(-1), 0.4754(0)	0.1263(0), 0.4742(0)
10	0.4655(-1), 0.2867(0)	0.5355(-1), 0.2958(0)
15	0.3760(-1), 0.2014(0)	0.3626(-1), 0.2061(0)
20	0.3237(-1), 0.1592(0)	0.3000(-1), 0.1610(0)
25	0.2792(-1), 0.1357(0)	0.2606(-1), 0.1363(0)
30	0.2393(-1), 0.1205(0)	0.2271(-1), 0.1206(0)

Table 6.20: Full, second Born matrix elements calculated using the closure approximation. Column one gives the results with no intermediate states included, columns two and three give the matrix elements calculated including the 2^1S and 2^2P intermediate states

Scattering		$200eV$	
angle	Byron and Joachain	$\Delta = 0.84245$	$\Delta = 1.45$
5	0.4338(0), 0.7969(0)	0.3303(0),0.8783(0)	0.3154(0),0.7245(0)
10	0.2467(0), 0.6281(0)	0.1894(0), 0.6411(0)	0.2927(0), 0.6260(0)
15	0.1546(0), 0.4789(0)	0.1315(0), 0.4712(0)	0.1997(0), 0.4923(0)
20	0.1112(0), 0.3728(0)	0.1052(0), 0.3625(0)	0.1374(0), 0.3831(0)
25	0.8974(-1), 0.3024(0)	0.9094(-1), 0.2944(0)	0.1018(0), 0.3077(0)
30	0.7786(-1), 0.2565(0)	0.8144(-1), 0.2512(0)	0.8167(-1), 0.2585(0)
		$300eV$	
5	0.2589(0), 0.6605(0)	0.1785(0), 0.6825(0)	0.1729(0), 0.5892(0)
10	0.1237(0), 0.4627(0)	0.1039(0), 0.4621(0)	0.1910(0), 0.5090(0)
15	0.7766(-1), 0.3319(0)	0.7608(-1), 0.3279(0)	0.1202(0),0.3680(0)
20	0.5999(-1), 0.2548(0)	0.6294(-1), 0.2512(0)	0.7816(-1),0.2703(0)
25	0.5142(-1), 0.2095(0)	0.5476(-1), 0.2071(0)	0.5661(-1),0.2136(0)
30	0.4579(-1), 0.1818(0)	0.4842(-1), 0.1804(0)	0.4486(-1),0.1811(0)
		$400eV$	
5	0.1676(0), 0.5562(0)	0.1150(0), 0.5579(0)	0.1344(0),0.5123(0)
10	0.7459(-1), 0.3604(0)	0.7049(-1), 0.3627(0)	0.1463(0),0.4380(0)
15	0.4972(-1), 0.2527(0)	0.5291(-1), 0.2527(0)	0.8372(-1),0.2930(0)
20	0.4060(-1), 0.1956(0)	0.4389(-1), 0.1945(0)	0.5139(-1),0.2071(0)
25	0.3542(-1), 0.1637(0)	0.3767(-1), 0.1626(0)	0.3604(-1),0.1636(0)
30	0.3130(-1), 0.1441(0)	0.3259(-1), 0.1432(0)	0.2785(-1),0.1404(0)
		$500eV$	
5	0.1154(0), 0.4766(0)	0.8375(-1), 0.4750(0)	0.1286(0),0.4763(0)
10	0.5106(-1), 0.2938(0)	0.5316(-1), 0.2998(0)	0.1194(0),0.3884(0)
15	0.3623(-1), 0.2048(0)	0.4008(-1), 0.2063(0)	0.6201(-1),0.2412(0)
20	0.3042(-1), 0.1605(0)	0.3294(-1), 0.1599(0)	0.3600(-1),0.1664(0)
25	0.2645(-1), 0.1361(0)	0.2776(-1), 0.1352(0)	0.2439(-1),0.1324(0)
30	0.2298(-1), 0.1205(0)	0.2352(-1), 0.1197(0)	0.1840(-1),0.1148(0)

Table 6.21: Individual contributions to the second Born matrix elements

	Byron and Joachain	$\Delta = 0.84245$	$\Delta = 1.45$
Scattering Angle = 5, Energy = $200eV$			
2^1S	0.0000(0),0.0000(0)	-0.2747(-4), 0.1062(-4)	-0.2085(-3), 0.1179(-3)
2^1P	0.0000(0),0.0000(0)	-0.2088(-1), -0.1034(-1)	-0.1348(0), -0.4208(-1)
$f_C^{(1)}$	0.4338(0), 0.7969(0)	0.3512(0), 0.8887(0)	0.4504(0), 0.7665(0)
Scattering Angle = 30, Energy = $200eV$			
2^1S	0.0000(0),0.0000(0)	-0.1439(-4), 0.2694(-5)	-0.1141(-3), 0.3834(-4)
2^1P	0.0000(0),0.0000(0)	0.4693(-3), 0.2207(-3)	0.3922(-2), -0.1285(-3)
$f_C^{(1)}$	0.7786(-1), 0.2565(0)	0.8098(-1), 0.2510(0)	0.7786(-1), 0.2586(0)
Scattering Angle = 5, Energy = $500eV$			
2^1S	0.0000(0),0.0000(0)	-0.1079(-4), 0.2479(-5)	-0.8583(-4), 0.2804(-4)
2^1P	0.0000(0),0.0000(0)	0.1268(-2), -0.3470(-3)	0.2449(-2), 0.2085(-2)
$f_C^{(1)}$	0.1154(0), 0.4766(0)	0.8250(-1), 0.4754(0)	0.1263(0), 0.4742(0)
Scattering Angle = 30, Energy = $500eV$			
2^1S	0.0000(0),0.0000(0)	-0.2200(-5), 0.5640(-7)	-0.1807(-4), 0.9613(-6)
2^1P	0.0000(0),0.0000(0)	-0.4076(-3), -0.8301(-3)	-0.4290(-2), -0.5762(-2)
$f_C^{(1)}$	0.2298(-1), 0.1205(0)	0.2393(-1), 0.1205(0)	0.2271(-1), 0.1206(0)

diate states included in the calculation, from eqn 6.66. Also given are the Byron and Joachain results from table 6.11. The three sets of results are in reasonable agreement, with the greatest discrepancies being at low energies and small scattering angles. These differences can be explained by considering the individual contributions to the results of table 6.20. Table 6.21 gives the individual terms in the calculation of the second Born matrix elements for a number of energies and scattering angles.

The terms 2^1S and 2^1P from table 6.21 are calculated by (see eqn 6.66),

$$\begin{aligned} 2^1S &= I_b(2^1S; k_{2^1S}) - I_b(2^1S; \bar{k}) \\ 2^1P &= \sum_{m=1}^{3} \left(I_b(2^1P_m; k_{2^1P}) - I_b(2^1P_m; \bar{k}) \right). \end{aligned} \tag{6.78}$$

From table 6.21 it is evident that the 2^1S state is not significantly influencing the overall second Born matrix elements, throughout the angular and energy range considered. The 2^1P terms with $\Delta = 0.84245$ are, not unexpectedly, rather smaller than the $\Delta = 1.45$ results. $\Delta = 0.84245$ is much closer to the intermediate state momentum k_{2^1P}, thus the differences

Table 6.22: First Born amplitudes for elastic scattering from the 1^1S state of helium

Scattering angle	$200eV$	$300eV$	$400eV$	$500eV$
5	-0.7771(0)	-0.7701(0)	-0.7632(0)	-0.7564(0)
10	-0.7368(0)	-0.7121(0)	-0.6889(0)	-0.6670(0)
15	-0.6781(0)	-0.6323(0)	-0.5920(0)	-0.5564(0)
20	-0.6099(0)	-0.5462(0)	-0.4941(0)	-0.4508(0)
25	-0.5401(0)	-0.4646(0)	-0.4070(0)	-0.3618(0)
30	-0.4740(0)	-0.3928(0)	-0.3348(0)	-0.2912(0)

defined in eqn 6.78 are expected to be smaller than the $\Delta = 1.45$ case. The first Born amplitudes must also be taken into account when calculating the total second Born scattering amplitude. Table 6.22 gives the first Born amplitudes corresponding to the scattering angles and energies of the second Born matrix elements, generated above.

The first Born amplitudes from table 6.22 are comparable or greater in magnitude to the second Born matrix elements from table 6.20, with the relative importance of the second order terms decreasing with increasing energy as expected for a perturbation expansion. The second Born matrix elements are larger, relative to the first Born amplitudes, at smaller angles which has been attributed to the importance of target polarization for small angle scattering [57].

Because of the relative simplicity of the $2^1P \leftarrow 1^1S$ first Born scattering amplitudes, no significant simplification can be made by fitting to a function of the form of eqn 6.59 and then calculating the second Born matrix elements. Inclusion of further intermediate states in the closure expression for the second Born matrix elements, eqn 6.35, requires no additional computational techniques. Approximate $3^1S, 3^1P$ and 3^1D helium wave functions have been given by Goldberg and Clogston [84], or tables of generalised oscillator strengths for states up to 4^1P are available [88, 86], which can be fitted, allowing the second Born matrix elements to be calculated. Through this body of work, we developed and tested numerical methods to calculate scattering amplitudes via the Born approximation. Chapter 7 details the attempts made to extend these ideas to non-spherically symmetric interaction potentials.

Table 6.23: Orbital exponents for the Gaussian basis used for the Schwinger potential scattering calculations

s functions	p_z functions	d_{z^2} functions
0.9673(2)	0.1500(1)	0.1500(1)
0.1461(2)	0.7500(0)	0.7500(0)
0.3304(1)	0.3000(0)	0.1000(-1)
0.8731(0)	0.1200(0)	
0.2445(0)	0.4800(-1)	
0.1358(0)	0.1000(-1)	
0.7547(-1)		
0.4193(-1)		
0.2329(-1)		
0.1294(-1)		

6.3 Potential Scattering Using the Schwinger Variational Principle

The Schwinger variational principle (see chapter 5) was used to calculate the scattering amplitude from two static potentials. The first of these was a simple Gaussian potential, $V(\mathbf{r}) = -\exp(-r^2)$. Accurate scattering amplitudes for this potential have been published by Holt and Santoso [95] using the *Fredholm Integral Method* and via a Runge-Kutta procedure, so this was a useful starting point for the development of out numerical tools.

The Schwinger expression for the transition matrix elements is, from eqn 5.8

$$T_{\mathbf{k_2};\mathbf{k_1}} = \frac{\langle \phi_{\mathbf{k_2}} | V | \phi^{(+)}_{\mathbf{k_1}} \rangle \langle \phi^{(-)}_{\mathbf{k_2}} | V | \phi_{\mathbf{k_1}} \rangle}{\langle \phi^{(-)}_{\mathbf{k_2}} | V - V G_0 V | \phi^{(+)}_{\mathbf{k_1}} \rangle}. \tag{6.79}$$

The scattering orbitals $\phi^{(+)}_{\mathbf{k_1}}(\mathbf{r})$ and $\phi^{(-)}_{\mathbf{k_2}}(\mathbf{r})$ were expanded in a basis of Gaussian functions, $\{g_i\}$ taken from the paper of McKoy and Watson [23], augmented by three d functions. Table 6.23 gives the orbital exponents for the basis used. Only the z orbitals of p symmetry, and the z^2 orbitals of d symmetry contribute to the resulting equations which simplifies the basis.

With the scattering orbitals expanded in the basis $\{g_i\}$, eqn 6.79 becomes

$$T_{\mathbf{k_2},\mathbf{k_1}} = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \phi_{\mathbf{k_2}} | V | g_i \rangle [D_{ij}]^{-1} \langle g_j | V | \phi_{\mathbf{k_1}} \rangle, \tag{6.80}$$

where

Table 6.24: Scattering amplitudes calculated via the Schwinger variational principle and the Fredholm integral method, for the Gaussian potential $V(\mathbf{r}) = -\exp(-r^2)$

$\lvert\mathbf{k}_1\rvert$ *a.u.*	Scattering angle	Schwinger	Fredholm
0.447	0	0.5864(0), 0.1384(0)	0.5830(0), 0.1390(0)
	90	0.5389(0), 0.1382(0)	0.5380(0), 0.1380(0)
	180	0.5000(0), 0.1379(0)	0.4970(0), 0.1380(0)
1.0	0	0.4597(0), 0.1033(0)	0.4720(0), 0.1040(0)
	90	0.2762(0), 0.9701(-1)	0.2830(0), 0.9600(-1)
	180	0.1582(0), 0.8813(-1)	0.1660(0), 0.8900(-1)
2.0	0	0.3353(0), 0.1804(-1)	0.4480(0), 0.5000(-1)
	90	0.7996(-1), 0.1337(-1)	0.5200(-1), 0.2000(-1)
	180	-0.2642(-1), 0.6230(-1)	0.4000(-3), 0.4500(-2)

$$D_{ij} = \langle g_j | V - V G_0 V | g_i \rangle. \tag{6.81}$$

The scattering amplitudes corresponding to the transition matrix elements $T_{\mathbf{k_2},\mathbf{k_1}}$ are given simply by, $f(\mathbf{k_2},\mathbf{k_1}) = -1/(4\pi) T_{\mathbf{k_2},\mathbf{k_1}}$.

For the Gaussian potential $V(\mathbf{r}) = -\exp(-r^2)$, the three matrix elements required to evaluate eqn 6.80 are

- $\langle \phi_{\mathbf{k_2}} | V | g_i \rangle$ and $\langle g_j | V | \phi_{\mathbf{k_1}} \rangle$ which when written out explicitly are simply the Fourier transforms of the Gaussians, $g_{i/j}$ with the orbital exponent increased by 1.

- $\langle g_j | V | g_i \rangle$ which reduces to, on combination of the three Gaussian functions, to the integral over a single Gaussian centered at the origin, which can easily be evaluated.

- $\langle g_j | V G_0 V | g_i \rangle$ which becomes, on substitution of V, the Gaussian matrix element of the two particle Green's operator. These matrix elements have been evaluated for general Cartesian Gaussian functions up to d symmetry by Levin *et al.* [96] (see appendix I)

Table 6.24 gives the scattering amplitudes for scattering from the Gaussian potential $V(\mathbf{r}) = -\exp(-r^2)$, calculated using eqn 6.80, with the basis given in table 6.23. Also given are the Fredholm integral results of Holt and Santoso [95].

The results from table 6.24 show an increasing discrepancy between the accurate Fredholm and the Schwinger results, on increasing energy. This is attributed to the incompleteness of the basis used to expand the scattering orbitals. The Fredholm results are increasingly peaked in the forward direction on increasing energy, as expected. For the Schwinger principle to reproduce the highly peaked nature of the Fredholm results at energies above 1 $a.u.$ requires a basis containing higher order angular momentum functions. As noted, only functions of Σ symmetry contribute to eqn 6.80, so to improve the results, f_{z^3}, g_{z^4} etc. functions must be used. At high enough energies, the scattering orbitals $\phi^{(+)}_{\mathbf{k_1}}(\mathbf{r})$ and $\phi^{(-)}_{\mathbf{k_2}}(\mathbf{r})$ become oscillatory, so the use of simple Gaussian functions centered at the origin will become increasingly inadequate. There is thus a limit to the use of simple L^2 functions for the expansion of scattering orbitals.

6.3.1 Helium Scattering via the Schwinger Variational Theory

Electron-helium potential scattering amplitudes were also calculated using the Schwinger variational principle. The most conveniently way to describe the interaction potential is to use the static exchange potential for helium (see section 4.5.1). For elastic scattering, the static exchange potential for scattering from the ground state of helium is written

$$V^{\mathrm{He}}_{SE}(\mathbf{r}) = -\frac{2}{r} + 2J^{\mathrm{He}}_{1s}(\mathbf{r}) - K^{\mathrm{He}}_{1s}(\mathbf{r}) \tag{6.82}$$

The first term is the electron-nucleus interaction. $J_{1^1S}(\mathbf{r})$ is the coulomb part of the interaction potential, given by

$$J^{\mathrm{He}}_{1s}(\mathbf{r}) = \int d\tau_1 \, \phi^{\mathrm{He}*}_{1s}(\mathbf{r_1})\phi^{\mathrm{He}}_{1s}(\mathbf{r_1})\frac{1}{|\mathbf{r}-\mathbf{r_1}|}. \tag{6.83}$$

If the matrix element to be evaluated is $\langle\phi_i|V^{\mathrm{He}}_{SE}|\phi_j\rangle$, the final term of eqn 6.82 represents the exchange contribution, and can be written,

$$K^{\mathrm{He}}_{1s}(\mathbf{r}) = \frac{\phi^{\mathrm{He}}_{1s}(\mathbf{r})}{\phi_j(\mathbf{r})}\int d\tau_1 \, \phi^{\mathrm{He}*}_{1s}(\mathbf{r_1})\phi_j(\mathbf{r_1})\frac{1}{|\mathbf{r}-\mathbf{r_1}|}. \tag{6.84}$$

The advantage of using this nomenclature, is the Schwinger variational expression for the transition matrix elements reduces to the equivalent one particle equation (see eqn 6.79),

$$T_{\mathbf{k_2},1^1S;\mathbf{k_1},1^1S} = \frac{\langle \phi_{\mathbf{k_2}} | V_{SE}^{\mathrm{He}} | \phi_{\mathbf{k_1}}^{(+)} \rangle \langle \phi_{\mathbf{k_2}}^{(-)} | V_{SE}^{\mathrm{He}} | \phi_{\mathbf{k_1}} \rangle}{\langle \phi_{\mathbf{k_2}}^{(-)} | V_{SE}^{\mathrm{He}} - V_{SE}^{\mathrm{He}} G_0 V_{SE}^{\mathrm{He}} | \phi_{\mathbf{k_1}}^{(+)} \rangle}. \tag{6.85}$$

As with the Gaussian potential, the scattering orbitals $\phi_{\mathbf{k_1}}^{(+)}$ and $\phi_{\mathbf{k_2}}^{(-)}$ were expanded using the basis given in table 6.23 leading to the same expression for the transition matrix elements as eqn 6.80, with V replaced by V_{SE}^{He}. Using Gaussian functions to expand the target helium orbital, $\phi_{1s}^{\mathrm{He}}(\mathbf{r})$ means the matrix elements over the interaction potential can be expresses as analytic functions. The helium $1s$ orbital was approximated by the same five function expansion used for the Born calculations. Table 6.1 gives the exponents and expansion coefficients for the $\phi_{1s}^{\mathrm{He}}(\mathbf{r})$ orbital.

The integrals required for the calculation of the scattering amplitudes for the helium, static exchange case are

- Bound-free matrix elements of the interaction potential, written $\langle \phi_{\mathbf{k}} | V_{SE}^{\mathrm{He}} | g_i \rangle$. From the explicit expression for the static exchange potential, eqn 6.82, the two integrals required are

$$\int d\tau e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{r} g_i(\mathbf{r}) \tag{6.86}$$

and

$$\int d\tau_1 \int d\tau_2 e^{i\mathbf{k}\cdot\mathbf{r}_1} g_i(\mathbf{r_1}) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} g_j(\mathbf{r_2}) g_k(\mathbf{r_2}) \tag{6.87}$$

($g_i(\mathbf{r})$ represents a general Gaussian function). These integrals have been evaluated by McKoy and Watson [23]. The individual integrals for s, p_z and d_{z^2} symmetries are given in appendix J

- Bound-bound matrix elements of the interaction potential, written $\langle g_i | V_{SE}^{\mathrm{He}} | g_j \rangle$. These are standard integrals required for bound state calculations. For simple s, p and d functions all centered at the origin, these integrals are not difficult to evaluate [97].

- Second Born like matrix elements of the Green's function, $\langle g_i | V_{SE}^{\mathrm{He}} G_0 V_{SE}^{\mathrm{He}} | g_j \rangle$. The spectral representation of this matrix element is

$$\langle g_i|V_{SE}^{\mathrm{He}}G_0V_{SE}^{\mathrm{He}}|g_j\rangle = \lim_{\eta\to 0}\int d\mathbf{k}\frac{\langle g_i|V_{SE}^{\mathrm{He}}|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|V_{SE}^{\mathrm{He}}|g_j\rangle}{k^2-k_0^2-i\eta}$$
$$= \int d\mathbf{k}\frac{\langle g_i|V_{SE}^{\mathrm{He}}|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|V_{SE}^{\mathrm{He}}|g_j\rangle}{k^2-k_0^2}$$
$$+i\pi k_0\int d\Omega_\mathbf{k}\langle g_i|V_{SE}^{\mathrm{He}}|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|V_{SE}^{\mathrm{He}}|g_j\rangle_{|\mathbf{k}|=k_0} \tag{6.88}$$

The explicit expressions for the bound-free matrix elements (see appendix J), can be written in short form as

$$\langle s|V_{SE}^{\mathrm{He}}|\phi_\mathbf{k}\rangle = A_1(k) \tag{6.89}$$

$$\langle p_z|V_{SE}^{\mathrm{He}}|\phi_\mathbf{k}\rangle = k_z A_2(k) \tag{6.90}$$

$$\langle d_{z^2}|V_{SE}^{\mathrm{He}}|\phi_\mathbf{k}\rangle = A_3(k) + k_z^2 A_4(k) \tag{6.91}$$

The angular part of the final integral over $\mathbf{k}$ in eqn 6.88 can thus be easily completed, leaving a principle value radial integral,

$$I_P = \int_0^\infty \frac{k^2 A_i(k)A_j(k)}{k^2-k_0^2}. \tag{6.92}$$

This integral was completed numerically using Gauss-Legendre quadrature over the range $0 \le k \le 2k_0$, and Gauss-Laguerre over the semi-infinite range $2k_0 \le k \le \infty$. If the first integral, $0 \le k \le 2k_0$, has quadrature points symmetric about $k = k_0$, no problem arises due to the singularity at that point, in the numerical integration. This method was preferred over the integration methods described in section 7.3.3 as it does not involve any transformation of the k coordinate, which becomes problematic when k_0 is small. This numerical integration scheme was tested by evaluating the Gaussian matrix elements of the Green's function and comparing with the analytic results of McKoy *et al* [23].

Table 6.25: Scattering amplitudes calculated via the Schwinger variational principle, for scattering from the ground state, static exchange potential of helium

k_0	Scattering angle	$f_{Schwinger}$
	0	0.1255(1), 0.1575(-2)
0.001	90	0.1255(1), 0.1575(-2)
	180	0.1255(1), 0.1575(-2)
	0	0.1257(1), 0.1580(-1)
0.01	90	0.1257(1), 0.1580(-1)
	180	0.1257(1), 0.1580(-1)
	0	0.1228(1), 0.1531(0)
0.1	90	0.1228(1), 0.1531(0)
	180	0.1227(1), 0.1531(0)
	0	0.1154(1), 0.2811(0)
0.2	90	0.1152(1), 0.2811(0)
	180	0.1149(1), 0.2811(0)
	0	0.8518(0), 0.4205(0)
0.5	90	0.8148(0), 0.4203(0)
	180	0.7778(0), 0.4200(0)
	0	0.5096(0), 0.2883(0)
1.0	90	0.4525(0), 0.2872(0)
	180	0.3953(0), 0.2883(0)

Table 6.25 gives the Schwinger scattering amplitudes for potential scattering from the ground state, static exchange potential of helium.

The calculations were taken down to very low energies because there are well defined limits of the amplitudes as $k_0 \rightarrow 0$. The real part of the amplitude tends to a constant and becomes isotropic in the scattering angle. The imaginary part becomes linear in k_0 and also becomes isotropic in the scattering angle.

Results from this section demonstrate our ability to calculate potential scattering amplitudes via the Schwinger variational principle. The second Born like matrix elements were approximated by the single term (from the spectral representation of the Green's function),

$$\begin{aligned}\langle \Phi^{(-)}_{\mathbf{k_2}} | V G_0 V | \Phi^{(+)}_{\mathbf{k_1}} \rangle &\approx \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{\langle \Phi^{(-)}_{\mathbf{k_2}} | V | \psi_{1^1S} \phi_{\mathbf{k}} \rangle \langle \psi_{1^1S} \phi_{\mathbf{k}} | V | \Phi^{(+)}_{\mathbf{k_1}} \rangle}{k^2 - k_0^2 - i\eta} \\ &= I_b(1^1S; k_0) \end{aligned} \tag{6.93}$$

The numerical procedures used to calculate this identity can be immediately extended to calculate additional $I_b(i; k_i)$ integrals, where i is an excited state of the helium atom. These are the terms required for the calculation of scattering amplitudes beyond the static exchange potential, (see section 5.3.1). The ability to calculate these terms allows pseudostate calculations [52] to be carried out, and allows the use of the closure approximation to estimate the second Born like matrix elements. These ideas are developed further in chapter 8.

Chapter 7

Electron-Molecular Hydrogen Scattering

A number of additional points arise in the calculation of scattering data from non-spherically symmetric potentials. For electron-helium scattering, the incident and final free electron momentum vectors, $\mathbf{k_1}$ and $\mathbf{k_2}$ respectively, are defined relative to a center of mass frame of the helium target. The target itself does not have any geometrical structure that depends on orientation, and so the orientation of the reference frame can be chosen arbitrarily. For diatomic molecular targets, $\mathbf{k_1}$ and $\mathbf{k_2}$ obviously must be defined relative to interatomic vector. This requires two additional parameters to fully specify the scattering geometry. For polyatomics, the three *Euler angles* are required to determine the orientation of the molecule with respect to the scattering vectors.

7.1 The First Born Scattering Amplitudes

In this thesis, Gaussian functions are used exclusively to expand molecular orbitals. These are the function of choice for bound state polyatomic calculations [19] due to the fact that two Gaussian functions of the same argument, centered at two points $\mathbf{A}$ and $\mathbf{B}$, can be written as a single Gaussian centered on the line of intersection $\overline{\mathbf{AB}}$. More specifically, it can easily be shown that

$$e^{-\alpha(\mathbf{r}-\mathbf{A})^2}e^{-\beta(\mathbf{r}-\mathbf{B})^2} = e^{-\gamma(\mathbf{A}-\mathbf{B})^2}e^{-\delta(\mathbf{r}-\mathbf{C})^2} \tag{7.1}$$

where

$$\gamma = \frac{\alpha\beta}{\alpha+\beta} \qquad \delta = \alpha+\beta \qquad \text{and} \qquad \mathbf{C} = \frac{\alpha\mathbf{A}+\beta\mathbf{B}}{\alpha+\beta}. \tag{7.2}$$

This greatly simplifies the bound state multicenter integrals required, and can be similarly exploited in scattering calculations.

The ground state of molecular hydrogen is the $X^1\Sigma_g^+$ state and is approximated by a doubly occupied molecular orbital labeled σ_{1g}. The orbital is further approximated by a linear combination of Gaussian s-functions centered on the two atomic centers. The $X^1\Sigma_g^+$ state of H_2 is now

$$\Psi_{X^1\Sigma_g^+}(\mathbf{r_1},\mathbf{r_2}) \approx \sigma_{1g}(\mathbf{r_1})\sigma_{1g}(\mathbf{r_2})[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \tag{7.3}$$

and

$$\sigma_{1g}(\mathbf{r}) = \sum_{i=1}^{N} N_\alpha c_{i,1g} e^{-\alpha(\mathbf{r}-\mathbf{A_i})^2}. \tag{7.4}$$

Evaluation of the first Born scattering amplitudes proceeds in the same manner as the amplitudes for helium scattering. The direct two electron integral required is only a slight modification of equation C.10. The solution of the full integral for general Gaussians is given by Watson and McKoy [23]. The one electron integral is simply given by Bethe's integral, eqn 6.5.

Table 7.1 gives the orbital exponents and coefficients for the basis sets used in the molecular hydrogen calculations. The exponents are uncontracted hydrogen basis sets taken from Poirier, Kari and Csizmadia [98]. The SCF coefficients were again obtained from a single point calculation using GAUSSIAN 92. The interatomic distance was fixed at the value of $1.40248a.u.$

The first Born scattering amplitudes calculated using the two basis sets of table 7.1, as a function of $\mathbf{K}$, are given in table 7.2 and fig 7-2. The scattering geometry is given in figure 7-1.

The two basis sets used to describe the σ_{1g} hydrogen orbital give very similar direct first

Table 7.1: Exponents and expansion coefficients for the approximation of the hydrogen σ_{1g} orbital as given by McKoy *et al.*

α_i	$c_i^{(6)}$	α_i	$c_i^{(10)}$
0.8264(2)	0.1670(-2)	0.1777(4)	0.3716(-4)
0.1241(2)	0.1297(-1)	0.2540(3)	0.3131(-3)
0.2824(1)	0.5817(-1)	0.5470(2)	0.1750(-2)
0.7977(0)	0.2034(0)	0.1502(2)	0.7419(-2)
0.2581(0)	0.2574(0)	0.4915(1)	0.2504(-1)
0.8989(-1)	0.9454(-1)	0.1795(1)	0.6687(-1)
		0.7107(0)	0.1772(0)
		0.3048(0)	0.1806(0)
		0.1380(0)	0.1451(0)
		0.6216(-1)	0.2355(0)

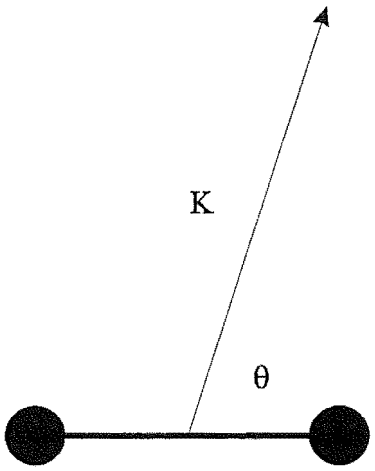


Figure 7-1: Geometry for the $e + H_2$ scattering system

Table 7.2: Elastic first Born scattering amplitudes for the scattering of electrons from molecular hydrogen using the 6 function and 10 function Gaussian basis sets

	$\theta = 0$		$\theta = 30$	
K	Gaussian(6)	Gaussian(10)	Gaussian(6)	Gaussian(10)
0.5	-0.1055(1)	-0.1053(1)	-0.1145(1)	-0.1144(1)
1.0	-0.6967(0)	-0.6966(0)	-0.8118(0)	-0.8117(0)
1.5	-0.3254(0)	-0.3255(0)	-0.4591(0)	-0.4592(0)
2.0	-0.4563(-1)	-0.4554(-1)	-0.1825(0)	-0.1824(0)
2.5	0.1269(0)	0.1269(0)	0.1911(-2)	0.1958(-2)
3.0	0.2128(0)	0.2129(0)	0.1103(0)	0.1103(0)
3.5	0.2386(0)	0.2386(0)	0.1644(0)	0.1643(0)
4.0	0.2260(0)	0.2259(0)	0.1818(0)	0.1818(0)
4.5	0.1912(0)	0.1912(0)	0.1758(0)	0.1758(0)
5.0	0.1459(0)	0.1459(0)	0.1555(0)	0.1555(0)
5.5	0.9796(-1)	0.9797(-1)	0.1274(0)	0.1274(0)
6.0	0.5293(-1)	0.5294(-1)	0.9608(-1)	0.9608(-1)
6.5	0.1432(-1)	0.1432(-1)	0.6487(-1)	0.6486(-1)
7.0	-0.1587(-1)	-0.1586(-1)	0.3602(-1)	0.3602(-1)
7.5	-0.3681(-1)	-0.3680(-1)	0.1107(-1)	0.1107(-1)
8.0	-0.4866(-1)	-0.4866(-1)	-0.9070(-2)	-0.9072(-2)
8.5	-0.5232(-1)	-0.5232(-1)	-0.2399(-1)	-0.2399(-1)
9.0	-0.4922(-1)	-0.4922(-1)	-0.3368(-1)	-0.3369(-1)
9.5	-0.4108(-1)	-0.4108(-1)	-0.3850(-1)	-0.3851(-1)
10.0	-0.2976(-1)	-0.2976(-1)	-0.3904(-1)	-0.3904(-1)
	$\theta = 60$		$\theta = 90$	
0.5	-0.1327(1)	-0.1326(1)	-0.1419(1)	-0.1418(1)
1.0	-0.1050(1)	-0.1050(1)	-0.1173(1)	-0.1173(1)
1.5	-0.7477(0)	-0.7477(0)	-0.9029(0)	-0.9029(0)
2.0	-0.4971(0)	-0.4971(0)	-0.6765(0)	-0.6764(0)
2.5	-0.3131(0)	-0.3131(0)	-0.5069(0)	-0.5069(0)
3.0	-0.1848(0)	-0.1848(0)	-0.3851(0)	-0.3852(0)
3.5	-0.9708(-1)	-0.9709(-1)	-0.2983(0)	-0.2983(0)
4.0	-0.3763(-1)	-0.3762(-1)	-0.2357(0)	-0.2357(0)
4.5	0.2344(-2)	0.2346(-2)	-0.1899(0)	-0.1899(0)
5.0	0.2878(-1)	0.2878(-1)	-0.1557(0)	-0.1557(0)
5.5	0.4570(-1)	0.4570(-1)	-0.1297(0)	-0.1297(0)
6.0	0.5583(-1)	0.5582(-1)	-0.1095(0)	-0.1095(0)
6.5	0.6104(-1)	0.6103(-1)	-0.9368(-1)	-0.9367(-1)
7.0	0.6265(-1)	0.6265(-1)	-0.8098(-1)	-0.8097(-1)
7.5	0.6164(-1)	0.6164(-1)	-0.7067(-1)	-0.7067(-1)
8.0	0.5872(-1)	0.5872(-1)	-0.6220(-1)	-0.6219(-1)
8.5	0.5444(-1)	0.5444(-1)	-0.5515(-1)	-0.5515(-1)
9.0	0.4923(-1)	0.4923(-1)	-0.4923(-1)	-0.4923(-1)
9.5	0.4342(-1)	0.4342(-1)	-0.4421(-1)	-0.4421(-1)
10.0	0.3729(-1)	0.3729(-1)	-0.3991(-1)	-0.3992(-1)

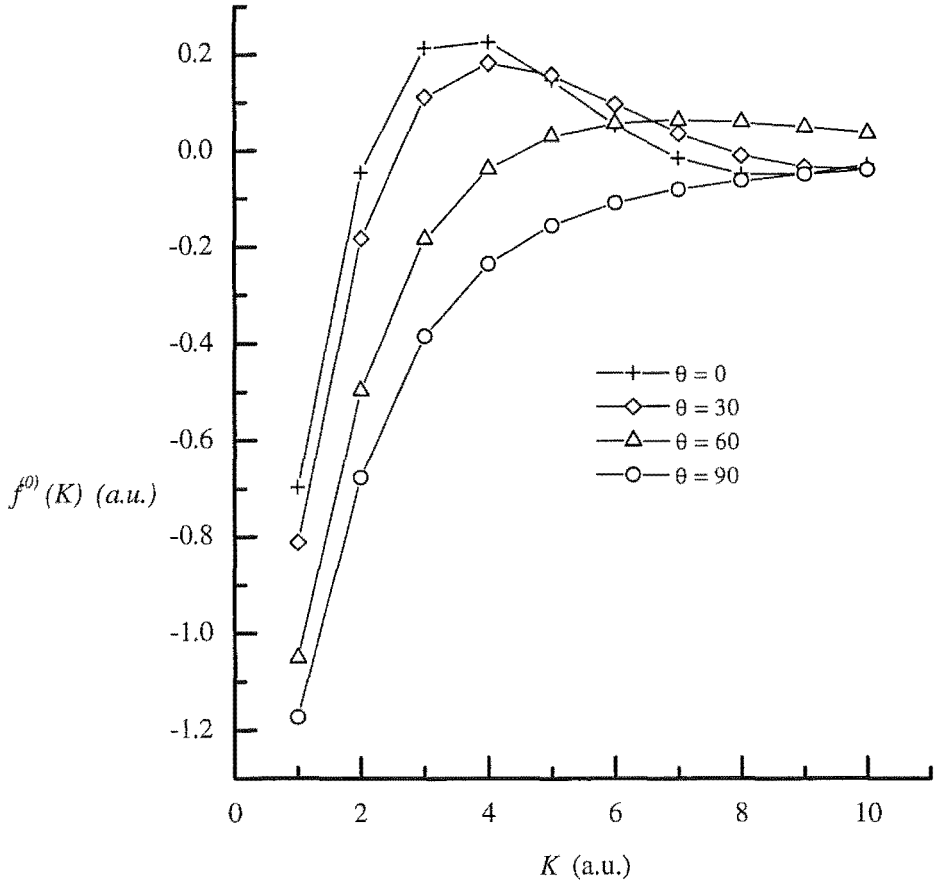


Figure 7-2: Elastic first Born H_2 scattering amplitudes

Born scattering amplitudes. The $\theta = 90$ results begin to follow the helium results from table 6.2 above $7.5 a.u.$ This is to be expected as the electron-nuclei scattering begins to dominate above this energy and the $\theta = 90$ geometry has the same electron-nuclei amplitude as helium. The nuclear term is

$$\frac{e^{i\mathbf{K}\cdot\mathbf{A}} + e^{-i\mathbf{K}\cdot\mathbf{A}}}{K^2} \tag{7.5}$$

so for the $\theta = 90$ geometry this reduces to the helium term, $2/K^2$. For $\mathbf{K}$ not perpendicular to $\mathbf{A}$ the oscillatory nature of the amplitudes becomes evident as θ becomes smaller and K becomes larger.

7.2 The Second Born Matrix Elements

Calculation of the second Born Matrix elements for electron scattering from molecular hydrogen, initially proceeds in exactly the same manner as the calculation of the second Born amplitudes for helium from section 6.2. Applying the closure approximation, including only the ground state in the summation over the intermediate states and using the ground state wave function approximated as in eqn 7.3, leads to the expression for the second Born matrix elements

$$\begin{aligned}
&\langle \psi_{X^1\Sigma_g^+} | V G_0^+ V | \psi_{X^1\Sigma_g^+} \rangle \approx \\
&\lim_{\eta\to 0^+} \int \frac{d\mathbf{k}}{(k^2 - k_0^2 - i\eta)} f^{(0)}(\mathbf{k_2}, X^1\Sigma_g^+; \mathbf{k_1}, X^1\Sigma_g^+) f^{(0)}(\mathbf{k_2}, X^1\Sigma_g^+; \mathbf{k_1}, X^1\Sigma_g^+) \\
&\lim_{\eta\to 0^+} \int \frac{d\mathbf{k}}{(k^2 - \bar{k}^2 - i\eta)} f^{(0)}(\mathbf{k_2}, X^1\Sigma_g^+; \mathbf{k_1}, X^1\Sigma_g^+) f^{(0)}(\mathbf{k_2}, X^1\Sigma_g^+; \mathbf{k_1}, X^1\Sigma_g^+) \\
&+ \lim_{\eta\to 0^+} \int \frac{d\mathbf{k}}{(k^2 - \bar{k}^2 - i\eta)} \left(\frac{K^2}{K_1^2 K_2^2} f^{(0)}(\mathbf{k_2}, X^1\Sigma_g^+; \mathbf{k_1}, X^1\Sigma_g^+) \right. \\
&\left. - \frac{1}{K_1^2} f^{(0)}(\mathbf{k_2}, X^1\Sigma_g^+; \mathbf{k}, X^1\Sigma_g^+) - \frac{1}{K_2^2} f^{(0)}(\mathbf{k}, X^1\Sigma_g^+; \mathbf{k_1}, X^1\Sigma_g^+) \right)
\end{aligned} \tag{7.6}$$

For the atomic case, the first Born amplitudes are fitted using a non-linear function of the form

$$\sum_i \frac{a_i}{(K^2+b_i^2)^{n_i}} \frac{Y_{LM}(\hat{\mathbf{K}})}{K^L} \tag{7.7}$$

which allows the resulting integrals of eqn 7.6 to be evaluated analytically. Unfortunately, the molecular first Born scattering amplitudes cannot be fitted to any degree, to a function of the form of eqn 7.7 or indeed any function with the simple form $A(r)P_L(\cos\theta)$. The factor $\exp(\pm i\mathbf{K}\cdot\mathbf{A})$ present in the first Born amplitudes must be included. This precludes the use of ideas similar to those used in the atomic case.

7.3 Numerical Evaluation of Second Born Matrix Elements

Fitting the first Born amplitudes to functions which allow the second Born matrix elements to be calculated analytically, does not appear to be a viable approach to calculating these matrix elements for molecular targets. Using Gaussian functions to expand the molecular orbitals means the first Born matrix elements can be calculated in closed form as a function of the vectors $\mathbf{k_1}$ and $\mathbf{k_2}$. Being able to efficiently calculating these terms, which are part of the integrand in the second Born integrals, means numerical estimation of the required integral over $\mathbf{k}$ may be feasible.

Because results for helium were available (from chapter 6), numerical techniques were first applied to helium to ensure the two sets of results matched.

7.3.1 Numerical Integration Applied to Helium

Following eqn 7.6, the integrals to be evaluated are of the general form

$$\begin{aligned} I_b(0,\bar{k}) &= \lim_{\eta\to 0}\int \frac{d\mathbf{k}}{K_1^2K_2^2(k^2-\bar{k}^2-i\eta)} \\ &\quad \langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_2}\cdot\mathbf{r}}-1|\phi_{1s}^{\mathrm{He}}\rangle\langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_1}\cdot\mathbf{r}}-1|\phi_{1s}^{\mathrm{He}}\rangle \end{aligned} \tag{7.8}$$

and

$$I_c(\bar{k}) = \lim_{\eta\to 0}\int \frac{d\mathbf{k}}{K_1^2 K_2^2(k^2-\bar{k}^2-i\eta)} \langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K}\cdot\mathbf{r}} - e^{i\mathbf{K_2}\cdot\mathbf{r}} - e^{i\mathbf{K_1}\cdot\mathbf{r}} + 1|\phi_{1s}^{\mathrm{He}}\rangle. \tag{7.9}$$

$$\mathbf{K_1} = \mathbf{k_1} - \mathbf{k} \qquad \mathbf{K_2} = \mathbf{k} - \mathbf{k_2} \qquad \mathbf{K} = \mathbf{k_1} - \mathbf{k_2} \tag{7.10}$$

Considering the integral $I_b(0,\bar{k})$ first, the function

$$\begin{aligned} F(\mathbf{k_1},\mathbf{k_2};\mathbf{k}) &= \frac{1}{K_1^2 K_2^2}\langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_2}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}\rangle\langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K_1}\cdot\mathbf{r}} - 1|\phi_{1s}^{\mathrm{He}}\rangle \\ &= f^{(0)}(\mathbf{k_2},0;\mathbf{k},0)f^{(0)}(\mathbf{k},0;\mathbf{k_1},0) \end{aligned} \tag{7.11}$$

is a smooth function of the argument $\mathbf{k}$, so the integral reduces to the general form

$$I_b(0,\bar{k}) = \lim_{\eta\to 0}\int \frac{F(\mathbf{k_1},\mathbf{k_2};\mathbf{k})d\mathbf{k}}{k^2-\bar{k}^2-i\eta}. \tag{7.12}$$

Using the Cauchy integral theorem (see section 5.2.2), this becomes

$$I_b(0,\bar{k}) = P\int \frac{F(\mathbf{k_1},\mathbf{k_2};\mathbf{k})d\mathbf{k}}{k^2-\bar{k}^2} - i\pi\frac{\bar{k}}{2}\int d\Omega_{\mathbf{k}} F(\mathbf{k_1},\mathbf{k_2};\mathbf{k})_{|\mathbf{k}|=\bar{k}}. \tag{7.13}$$

P denotes the principal value integral and the second term is an angular integral over the function $F(\mathbf{k_1},\mathbf{k_2};\mathbf{k})$ evaluated at $|\mathbf{k}| = \bar{k}$.

7.3.2 Angular integration

The analytic solution of the second Born integral from appendix E, exploits the fact that the target functions are spherically symmetric to complete the two angular integrals. Similar ideas could be used here but are not because these techniques are to be applied to non-spherically symmetric targets, where the coordinate frame orientation cannot be chosen arbitrarily.

Changing to spherical polar coordinates, eqn 7.13 becomes

$$I_b(0,\bar{k}) = P\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} \frac{k^2 F(\mathbf{k_1},\mathbf{k_2};k,\theta,\phi)dk}{k^2-\bar{k}^2} - i\pi\frac{\bar{k}}{2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta F(\mathbf{k_1},\mathbf{k_2};\bar{k},\theta,\phi). \quad (7.14)$$

The numerical angular integrations were evaluated using Gaussian product formulas [99]. The integral over ϕ was performed using N point Gauss-Legendre quadrature and the integral over θ evaluated both with Gauss-Legendre and Labatto quadrature [100]. The θ integration is transformed to the coordinate $u = \cos\theta$ so

$$I_b(0,\bar{k}) = P\int_0^{2\pi} d\phi \int_{-1}^{1} du \int_0^{\infty} \frac{k^2 G(\mathbf{k_1},\mathbf{k_2};k,u,\phi)dk}{k^2-\bar{k}^2} - i\pi\frac{\bar{k}}{2}\int_0^{2\pi} d\phi \int_{-1}^{1} du\, G(\mathbf{k_1},\mathbf{k_2};\bar{k},u,\phi). \quad (7.15)$$

Labatto quadrature is a form of Gaussian quadrature which includes the end points of the range of integration. That is, the M point Labatto approximation to the integral $\int f(r)dr$ over the range $a \le r \le b$ is

$$\int_a^b f(r)dr \approx w_1 f(a) + w_M f(b) + \sum_{i=2}^{M-1} w_i f(r_i). \quad (7.16)$$

The advantage of using this integration scheme is that for an N point ϕ integration, the end points of the u integration only contribute a single term to the product summation rather than the N Gauss-Legendre points associated with the $u \neq 0$ term. Figure 7-3 shows for any $u \neq \pm 1$ there are N distinct vectors of varying ϕ but at the points $u = \pm 1$, the distinction between different ϕ is lost, so only a single term is added to the quadrature summation.

It can be shown that M point Labatto quadrature is the same order as $M-1$ point Gauss-Legendre quadrature. This means for numerical integration to the same order, the number of quadrature points required for the Gauss-Legendre product is $N(M-1)$ whereas the Labatto product is $N(M-2)+2$.

Tables 7.3 and 7.4 give the imaginary term from eqn 7.15, evaluated numerically by Gauss-

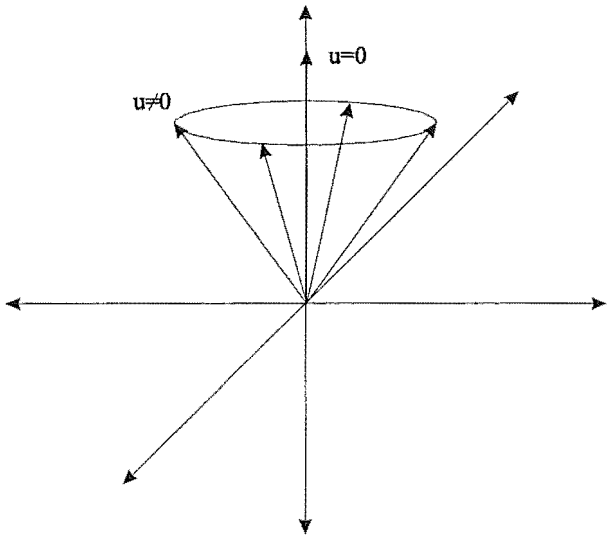


Figure 7-3: Geometry for the Labatto quadrature with $u = 0$ and $u \neq 0$

Table 7.3: Convergence as a function of number of angular quadrature points for the evaluation of the residue term in the second Born amplitude ($300eV$, $\bar{k} = 4.6956$)

	M = 8		M=12		M=16	
N	Labatto	Gauss	Labatto	Gauss	Labatto	Gauss
8	0.8325(-1)	0.8324(-1)	0.8324(-1)	0.8325(-1)	0.8325(-1)	0.8325(-1)
12	0.8333(-1)	0.8332(-1)	0.8333(-1)	0.8333(-1)	0.8333(-1)	0.8333(-1)
16	0.8333(-1)	0.8331(-1)	0.8332(-1)	0.8332(-1)	0.8332(-1)	0.8332(-1)
24	0.8333(-1)	0.8331(-1)	0.8332(-1)	0.8332(-1)	0.8332(-1)	0.8332(-1)

Legendre quadrature over the ϕ coordinate and both Gauss-Legendre and Labatto quadrature over the u coordinate. In both tables $|\mathbf{k_1}| = |\mathbf{k_2}| = 4.6956 a.u.$: ($300eV$) and the scattering angle is $\pi/2$. $\bar{k} = 4.6956 a.u.(300eV)$ in table 7.3 and $\bar{k} = 4.4102 a.u.$ in table 7.4. $\bar{k} = 4.4102 a.u.$ corresponds to the momentum obtained by using the closure energy of Byron and Joachain ($1.35 a.u.$) at $300eV$ (see section 6.2). The first Born matrix elements were calculated using the five function Gaussian ϕ_{1s}^{He} orbital of McKoy *et al.* (see table 6.1)

The same terms calculated analytically, are 0.8335(-1) and 0.4256(-1). The analytic results were calculated by fitting the first Born matrix elements $\langle \phi_{\mathbf{k_2}} \phi_{1s}^{\mathrm{He}} | V | \phi_{\mathbf{k_1}} \phi_{1s}^{\mathrm{He}} \rangle$ evaluated for the five function McKoy He($1s$) orbital, to the two function expansion similar to eqn 6.61. This was then used to evaluate the second Born matrix elements using eqn 6.58.

Table 7.4: Convergence as a function of number of angular quadrature points for the evaluation of the residue term in the second Born amplitude ($300eV$, $\bar{k} = 4.4102$)

	M=8		M=12		M=16	
N	Labatto	Gauss	Labatto	Gauss	Labatto	Gauss
8	0.4251(-1)	0.4250(-1)	0.4251(-1)	0.4251(-1)	0.4251(-1)	0.4251(-1)
12	0.4255(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)
16	0.4255(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)
24	0.4255(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)	0.4254(-1)

Table 7.5: Convergence as a function of number of angular quadrature points for the evaluation of the principal value term in the second Born amplitude ($300eV$, $\bar{k} = 4.4102$)

	M=8		M=12		M=16	
N	Labatto	Gauss	Labatto	Gauss	Labatto	Gauss
8	0.4320(-1)	0.4376(-1)	0.4350(-1)	0.4373(-1)	0.4360(-1)	0.4371(-1)
12	0.4317(-1)	0.4382(-1)	0.4350(-1)	0.4378(-1)	0.4362(-1)	0.4375(-1)
16	0.4317(-1)	0.4382(-1)	0.4350(-1)	0.4378(-1)	0.4361(-1)	0.4376(-1)
24	0.4318(-1)	0.4382(-1)	0.4350(-1)	0.4378(-1)	0.4362(-1)	0.4376(-1)
	M=24					
8	0.4366(-1)	0.4370(-1)				
12	0.4369(-1)	0.4373(-1)				
16	0.4369(-1)	0.4373(-1)				
24	0.4369(-1)	0.4373(-1)				

From tables 7.3 and 7.4, it can be seen that as expected, the Gauss-Legendre and Labatto quadratures of the same order, give essentially the same results. At this energy, the angular integrals have converged to within 1% at $N = 8, M = 8$.

The convergence properties of the angular integrals of I_b are constant over all scattering angles but weakly depends on the energy. At very low energies, the convergence of the angular integrals is slightly faster. At $|\mathbf{k_1}| = |\mathbf{k_2}| = 1.917 a.u.$ ($50eV$) the results corresponding to table 7.3 are fully converged to four significant figures at $N = M = 8$ for both Gauss-Legendre and Labatto quadrature. At $600eV$ the convergence is similar to the $300eV$ results.

The angular part of the closure integration $I_c(\bar{k})$, was treated in exactly the same manner as $I_b(0, \bar{k})$. Table 7.5 gives the imaginary part of the integral I_c, evaluated numerically as above for $|\mathbf{k_1}| = |\mathbf{k_2}| = 4.6956$ and $\bar{k} = 4.4102$.

The Gauss-Legendre results from table 7.5 are somewhat better than the Labatto numbers, the analytic result is 0.4376(-1).

The convergence properties of these integrals, does depend somewhat on the scattering

angle, at a scattering angle of $\pi/36$ the results have converged to less than 1% only at $M = 32$. The convergence in ϕ is not changed.

Table 7.6 gives the imaginary part of the full second Born matrix elements for varying numbers of quadrature points in the angular integrations. The angular integrations were performed using Gauss-Legendre quadrature. By studying the individual terms which contribute to the matrix elements, it can be seen that the imaginary part of the I_b terms have converged to four significant figures, for $M = 16$. The closure term, I_c requires $M = 32$ or 48. For small scattering angles, the I_c term contributes more to the full matrix elements than at larger scattering angles, which is reflected in the slower convergence of these terms.

In subsequent calculations, Gauss-Legendre quadrature over the variable u has been used rather than Labatto quadrature because it was considered easier to code in the programs used. No advantage in using Labatto quadrature was considered worth the more complicated code required. Further, the quadrature weights and points for Gauss-Legendre quadrature were more readily available. The scheme used in subsequent calculations was to calculate the I_b integrals using a $N = M = 16$ grid and a $N = 16, M = 32$ grid for the I_c integrals.

7.3.3 Radial Integration

A number of ways of treating the singular point in the radial integral of eqn 7.13 were investigated. The I_b integral,

$$I_b = P \int_0^\infty \frac{k^2 G(\mathbf{k_1}, \mathbf{k_2}; k, u, \phi) dk}{k^2 - \bar{k}^2}. \tag{7.17}$$

where $G(\mathbf{k_1}, \mathbf{k_2}; k, u, \phi)$ is a smooth function of k, is treated first.

SINC Quadrature

Utilizing the change of variable

$$t = k^2 \tag{7.18}$$

in eqn 7.17 leads to

Table 7.6: Imaginary part of the second Born matrix elements as a function of the number of angular quadrature points used in the numerical integrations

			$200eV, \theta = 10$		
			N		
M	8	12	16	24	32
8	0.6296(0)	0.6298(0)	0.6298(0)	0.6298(0)	0.6298(0)
12	0.6353(0)	0.6354(0)	0.6354(0)	0.6354(0)	0.6354(0)
16	0.6179(0)	0.6179(0)	0.6179(0)	0.6179(0)	0.6179(0)
24	0.6255(0)	0.6256(0)	0.6256(0)	0.6256(0)	0.6256(0)
32	0.6264(0)	0.6264(0)	0.6264(0)	0.6264(0)	0.6264(0)
48	0.6266(0)	0.6266(0)	0.6266(0)	0.6266(0)	0.6266(0)
			$\theta = 90$		
8	0.1236(0)	0.1238(0)	0.1238(0)	0.1238(0)	0.1238(0)
12	0.1235(0)	0.1236(0)	0.1236(0)	0.1236(0)	0.1236(0)
16	0.1235(0)	0.1236(0)	0.1236(0)	0.1236(0)	0.1236(0)
24	0.1234(0)	0.1235(0)	0.1235(0)	0.1236(0)	0.1235(0)
32	0.1234(0)	0.1235(0)	0.1235(0)	0.1235(0)	0.1235(0)
			$500eV, \theta = 10$		
8	0.3179(0)	0.3179(0)	0.3179(0)	0.3179(0)	0.3179(0)
12	0.3427(0)	0.3407(0)	0.3407(0)	0.3408(0)	0.3408(0)
16	0.2659(0)	0.2674(0)	0.2673(0)	0.2673(0)	0.2673(0)
24	0.2945(0)	0.2938(0)	0.2939(0)	0.2939(0)	0.2939(0)
32	0.2918(0)	0.2920(0)	0.2920(0)	0.2920(0)	0.2920(0)
48	0.2941(0)	0.2938(0)	0.2938(0)	0.2937(0)	0.2938(0)
			$\theta = 90$		
8	0.4946(-1)	0.4948(-1)	0.4948(-1)	0.4948(-1)	0.4948(-1)
12	0.4951(-1)	0.4953(-1)	0.4953(-1)	0.4953(-1)	0.4953(-1)
16	0.4951(-1)	0.4952(-1)	0.4952(-1)	0.4952(-1)	0.4952(-1)
24	0.4950(-1)	0.4952(-1)	0.4952(-1)	0.4952(-1)	0.4952(-1)
32	0.4950(-1)	0.4951(-1)	0.4951(-1)	0.4951(-1)	0.4951(-1)

$$I_b = P\int_0^\infty \frac{\sqrt{t}G(\mathbf{k_1},\mathbf{k_2},\sqrt{t},u,\phi)dt}{2(t-\bar{k}^2)} = \int_0^\infty \frac{H(t)dt}{t-t_0}. \tag{7.19}$$

The general integral, eqn 7.19 can be evaluated via SINC [1] quadrature [101]. There are a number of possible sinc quadratures which estimate Cauchy principal value integrals. The choices depend on the form of the function $H(t)$ and the range of integration. They are characterized by the fact that above a prescribed number of quadrature points, the error in the estimate of the integral, $Q_N^{(i)}$ is

$$Q_N^{(i)} \propto \exp(-\sqrt{N}) \tag{7.20}$$

where N is the number of quadrature points.

Gauss-Legendre Quadrature

Using the change of variable [102]

$$k = \zeta\frac{1+t}{1-t} \tag{7.21}$$

gives

$$dk = \zeta\frac{2}{(1-t)^2}. \tag{7.22}$$

This transformation maps the interval $k = 0 \rightarrow \infty$ to $-1 \leq t \leq 1$, with the center point of the t interval being $k = \zeta$.

The full integral, eqn 7.17 becomes

$$I_b = P\int_0^\infty \frac{k^2 G(\mathbf{k_1},\mathbf{k_2},k,u,\phi)}{k^2-\bar{k}^2}$$

[1] The SINC function $S(k,h)$ is defined as, $S(k,h)(z) = \sin[\pi(z-kh)/h]/(z-kh)$ where k is a positive integer and h is a positive real.

$$
\begin{aligned}
&= \int_{-1}^{1} dt \frac{\zeta^2 \left(\frac{1+t}{1-t}\right)^2 G\left(\mathbf{k_1}, \mathbf{k_2}, \zeta\left(\frac{1+t}{1-t}\right), u, \phi\right)}{\left(\zeta^2 \left(\frac{1+t}{1-t}\right)^2 - \bar{k}^2\right)} \frac{2\zeta}{(1-t)^2} \\
&= \int_{-1}^{1} dt \frac{\zeta^2 \left(\frac{1+t}{1-t}\right)^2 G\left(\mathbf{k_1}, \mathbf{k_2}, \zeta\left(\frac{1+t}{1-t}\right), u, \phi\right) 2\zeta}{(\zeta^2(1+t)^2 - \bar{k}^2(1-t)^2)}
\end{aligned} \tag{7.23}
$$

Now setting $\zeta = \bar{k}$ leads to

$$
I_b = -\int_{-1}^{1} dt \frac{\bar{k}\left(\frac{1+t}{1-t}\right)^2 G\left(\mathbf{k_1}, \mathbf{k_2}, \bar{k}\left(\frac{1+t}{1-t}\right), u, \phi\right)}{t} \tag{7.24}
$$

In this form the integral has a single discontinuity at $t = 0$. The function $G(\mathbf{k_1}, \mathbf{k_2}, k, u, \phi)$ is constrained at $k = \infty$ to be of order -2 or greater so the function

$$
\bar{k}\left(\frac{1+t}{1-t}\right)^2 G\left(\mathbf{k_1}, \mathbf{k_2}, \bar{k}\left(\frac{1+t}{1-t}\right), u, \phi\right) \tag{7.25}
$$

is finite at $t = 1$.

An integral of the form of eqn 7.24 can easily be estimated numerically, by symmetric Gauss-Legendre quadrature. Using a Gauss-Legendre quadrature over the range, $-1 \leq t \leq 1$ with an even number of quadrature points avoids the singular point at $t = 0$, and converges to the correct principle value integral.

Equivalent Quadrature

Utilizing the same change of variable as above,

$$
\begin{aligned}
I_b &= -\int_{-1}^{1} dt \frac{\bar{k}\left(\frac{1+t}{1-t}\right)^2 G\left(\mathbf{k_1}, \mathbf{k_2}, \bar{k}\left(\frac{1+t}{1-t}\right), u, \phi\right)}{2t} \\
&= -\int_{-1}^{1} dt \frac{(1+t)^2}{t} K(t),
\end{aligned} \tag{7.26}
$$

where $K(t)$ is a smooth function of t over the interval $-1 \leq t \leq 1$. The *equivalent quadrature* scheme [103], can be applied to this integral.

Using second order, Gauss-Jacobi quadrature points (t_i) and weights (w_i) such that

Table 7.7: Convergence of the radial integral in the evaluation of the principal value term of the second Born amplitudes for the three numerical methods described ($300eV$, $\bar{k} = 4.6956$)

N	Equivalent Quadrature	SINC	Gauss-Legendre
10	0.1296(-1)		
12	0.1286(-1)	0.1097(-1)	0.1276(-1)
16	0.1283(-1)	0.1178(-1)	0.1283(-1)
18	0.1283(-1)		
20	0.1283(-1)		
24		0.1245(-1)	0.1283(-1)
32		0.1267(-1)	0.1283(-1)
48		0.1280(-1)	0.1283(-1)

$$\int_{-1}^{1}(1+t)^2 f(t)dt \approx \sum_{i=1}^{N} w_i f(t_i), \tag{7.27}$$

the equivalent quadrature approximation to I_b is

$$I_b \approx \sum_{i=1}^{N} \frac{w_i K(t_i)}{t_i} + K(0)\left[\int_{-1}^{1} \frac{(1+t)^2 dt}{t} - \sum_{i=1}^{N} \frac{w_i}{t_i}\right]. \tag{7.28}$$

The first term in eqn 7.28 is just the usual N point approximation to the full function, treated as if there is no singular point present. The second two terms can be thought of as a constant times an exact integral over the range $-1 \leq t \leq 1$ minus the N point Gauss-Jacobi approximation over that range. Thus if the full function had no singularities these two contributions should cancel to the level of accuracy of the numerical integration.

Considering the first and last terms it can be seen that as $t_i \to 0$ these two terms cancel, so the abscissa for the numerical integration can be chosen independently. No additional error is introduced into the numerical estimate of the integral by the presence of the singular point at $t = 0$.

Tables 7.7 and 7.8 give the real part eqn 7.15 for a varying number of quadrature points, evaluated using the three numerical methods described. Again the scattering angle is $\pi/2$ and the energy is $4.6956 a.u.$ $\bar{k} = 4.6956$ for table 7.7, and 4.4102 for table 7.8.

The angular integrals were calculated using 16 point Gauss-Legendre quadratures in both the ϕ and u coordinates. The analytic values corresponding to tables 7.7 and 7.8 are 0.1281(-1)

Table 7.8: Convergence of the radial integral in the evaluation of the principal value term of the second Born amplitudes for the three numerical methods described ($300eV$, $\bar{k} = 4.4102$)

N	Equivalent Quadrature	SINC	Gauss-Legendre
10	0.1083(-1)		
12	0.1080(-1)	0.9646(-2)	0.1080(-1)
16	0.1080(-1)	0.1022(-1)	0.1081(-1)
18	0.1080(-1)		
20	0.1081(-1)		
24		0.1064(-1)	0.1081(-1)
32		0.1076(-1)	0.1081(-1)
48		0.1080(-1)	0.1081(-1)

and 0.1080(-1) respectively. All three methods are converging to the correct values. The SINC quadrature is the slowest to converge and was not considered useful as a method of calculation because of this. The equivalent quadrature integrals has slightly better convergence properties than the Gauss-Legendre quadrature, but is more difficult to program in a transparent way. These conclusions do not change when studying the results at differing energies and scattering angles.

The radial integral of $I_c(\bar{k})$ is complicated by the fact that the function

$$\frac{1}{K_1^2 K_2^2}\langle\phi_{1s}^{\mathrm{He}}|e^{i\mathbf{K}\cdot\mathbf{r}} - e^{i\mathbf{K_2}\cdot\mathbf{r}} - e^{i\mathbf{K_1}\cdot\mathbf{r}} + 1|\phi_{1s}^{\mathrm{He}}\rangle \tag{7.29}$$

is not a smooth function of k. In the region of $\mathbf{K_1} = 0$ and $\mathbf{K_2} = 0$, eqn 7.29 strongly depends on k. At these points, eqn 7.29 is finite. For elastic scattering, this problem can be removed by using similar techniques to the radial integrals above applied both at $k = \bar{k}$ and on the shell $|\mathbf{k}| = |\mathbf{k_1}| = |\mathbf{k_2}|$.

Defining $k_0 = |\mathbf{k_1}| = |\mathbf{k_2}|$, the semi-infinite interval $k = 0 \rightarrow \infty$ can be broken into two intervals,

Interval I

$$0 \leq k \leq \frac{k_0 + \bar{k}}{2} \tag{7.30}$$

This is transformed to the range $-1 \leq t \leq 1$ using the transform

Table 7.9: Convergence of I_c as a function of the number of quadrature points

N	$Re(I_c)$
8	0.1204(-1)
12	0.1198(-1)
16	0.1207(-1)
24	0.1209(-1)
32	0.1209(-1)

$$t = -\frac{1}{\alpha}\log\left(1 - \frac{k}{A}\right) \tag{7.31}$$

where

$$\alpha = -2\log\left(\frac{k_0 - \bar{k}}{2\bar{k}}\right) \quad \text{and} \quad A = \frac{k_0 + \bar{k}}{2(1 - \exp(-\alpha))} \tag{7.32}$$

which transforms $k = \bar{k}$ to $t = 0$. Gauss-Legendre quadrature was then employed to evaluate the integral over t.

Interval II

$$\frac{k_0 + \bar{k}}{2} \leq k \leq \infty \tag{7.33}$$

This was again transformed to the range $-1 \leq t \leq 1$, in this case using the transform

$$t = \frac{k - k_0}{k - \bar{k}} \tag{7.34}$$

from which $k = k_0$ transforms to $t = 0$. Gauss-Legendre quadrature was again employed to complete the integral.

The results of the radial integral of I_c are tabulated in table 7.9 for an energy of $4.6956 a.u.$ and $\bar{k} = 4.4102 a.u.$ The number of quadrature points N, refers to the number of points used in each of the two numerical integrals, over intervals I and II. The He($1s$) orbital is as above, and the angular integrals were completed using 32 and 16 point Gauss-Legendre quadrature in the u and ϕ angular coordinates respectively. The analytic value for this integral is 0.1208(-1).

Table 7.10 gives the principle value part of the full second Born matrix elements, as a function of the number of radial quadrature points used in the numerical integrations. The

Table 7.10: Real part of the second Born matrix elements as a function of the number of radial quadrature points used in the numerical integration

$200eV, \theta = 10$	
M	$\mathrm{Re}(f^{(1)})$
12	0.2411(0)
16	0.2407(0)
24	0.2400(0)
32	0.2398(0)
48	0.2398(0)
	$\theta = 90$
12	0.2940(-1)
16	0.2948(-1)
24	0.2948(-1)
32	0.2948(-1)
48	0.2948(-1)
$500eV, \theta = 10$	
12	0.4250(-1)
16	0.4311(-1)
24	0.4341(-1)
32	0.4343(-1)
48	0.4343(-1)
	$\theta = 90$
12	0.5125(-2)
16	0.5223(-2)
24	0.5273(-2)
32	0.5277(-2)
48	0.5278(-2)

I_b radial integrals were calculated using the transformation to the finite range $-1 \leq t \leq 1$ (eqn 7.21) and Gauss-Legendre quadrature. The number of quadrature points, M refers to the number of points used in the radial I_b integrals and the number of points used individually, in the two radial I_c integrals. From table 7.10 it was noted that the results for $M = 24$ were within 1% of the $M = 48$ results.

From these results the integration scheme given in table 7.11 was proposed for the estimation of the I_b and I_c integrals.

All Integrals were evaluated by Gauss-Legendre quadrature after suitable transformations of the original coordinates. Using this scheme requires 6144 basic function evaluations for each I_b integral and 24576 evaluations for the I_c integration. Each evaluation of the I_b function requires two calculations of first Born amplitudes. Similarly I_c requires three, so the total number of

Table 7.11: Quadrature scheme used for the numerical evaluation of the helium second Born matrix elements

	Intergal I_b			Integral I_c		
Coordinate	ϕ	u	k	ϕ	u	k
No. of quadrature points	16	16	24	16	32	24

first Born evaluations in this scheme is 98304 per scattering angle.

The results of this method are compared with analytic second Born amplitudes calculated for the five function Gaussian approximation to the He($1s$) orbital given by McKoy, in tables 7.12 and 7.13. The analytic amplitudes were calculated from a two term fit to the first Born amplitudes, similar to eqn 6.61.

At higher energy and small scattering angles, some discrepancy between the two sets of results is evident. Raising the number of radial quadrature points to 32 does not significantly alter the numerical results. This has been attributed to the real part of the closure integral I_c, which becomes increasingly peaked in the angular components as the energy increases, thus making it more difficult to estimate the integral numerically.

The results of the numerical integrations converge with satisfactory accuracy to the corresponding analytic results for helium, in the energy range we have considered. The discrepancy between the two is no greater than 2% over the entire range of energy and scattering angle.

7.3.4 Numerical Integration Applied to Hydrogen

Use of numerical techniques to estimate the integral over $\mathbf{k}$ in the second Born matrix elements, was developed so the closure approximation could be applied to molecular systems. Exactly the same methods as described in section 7.3.1 were used to calculate the second Born matrix elements for molecular hydrogen. The basis used to describe the σ_{1g} H_2 orbital was the six function basis described in table 7.1. The numerical integrations were carried out using the same methods as described above.

Because no alternative results were available for comparison, the numerical integrations were studied to ensure the results were at least converged. The integrations were performed as described in section 7.3. The two angular integrals and the radial integral were studied using a number different quadrature points.

Table 7.12: $200eV$ and $300eV$ second Born amplitudes calculated analytically from the two function fit to the first Born amplitudes and via the proposed numerical scheme

Scattering Angle	Analytic	Numerical
	$200eV$	
18	0.1247(0),0.4080(0)	0.1236(0),0.4093(0)
36	0.6874(-1),0.2198(0)	0.6964(-1),0.2207(0)
54	0.5089(-1),0.1687(0)	0.5084(-1),0.1695(0)
72	0.3820(-1),0.1420(0)	0.3808(-1),0.1427(0)
90	0.2953(-1),0.1230(0)	0.2948(-1),0.1235(0)
108	0.2387(-1),0.1091(0)	0.2384(-1),0.1094(0)
126	0.2026(-1),0.9920(-1)	0.2023(-1),0.9946(-1)
144	0.1805(-1),0.9266(-1)	0.1803(-1),0.9289(-1)
162	0.1686(-1),0.8894(-1)	0.1684(-1),0.8915(-1)
180	0.1648(-1),0.8773(-1)	0.1647(-1),0.8794(-1)
	$300eV$	
18	0.6532(-1),0.2792(0)	0.6421(-1),0.2796(0)
36	0.4029(-1),0.1593(0)	0.4106(-1),0.1602(0)
54	0.2746(-1),0.1232(0)	0.2742(-1),0.1237(0)
72	0.1915(-1),0.1004(0)	0.1908(-1),0.1008(0)
90	0.1413(-1),0.8425(-1)	0.1411(-1),0.8449(-1)
108	0.1112(-1),0.7298(-1)	0.1110(-1),0.7315(-1)
126	0.9287(-2),0.6532(-1)	0.9267(-2),0.6546(-1)
144	0.8202(-2),0.6039(-1)	0.8180(-2),0.6053(-1)
162	0.7625(-2),0.5764(-1)	0.7605(-2),0.5777(-1)
180	0.7444(-2),0.5676(-1)	0.7424(-2),0.5688(-1)

Table 7.13: $400eV$ and $500eV$ second Born amplitudes calculated analytically from the two function fit to the first Born amplitudes and via the proposed numerical scheme

	$400eV$	
18	0.4343(-1),0.2132(0)	0.4261(-1),0.2132(0)
36	0.2691(-1),0.1271(0)	0.2747(-1),0.1279(0)
54	0.1703(-1),0.9650(-1)	0.1701(-1),0.9693(-1)
72	0.1135(-1),0.7644(-1)	0.1131(-1),0.7666(-1)
90	0.8172(-2),0.6280(-1)	0.8156(-2),0.6294(-1)
108	0.6343(-2),0.5362(-1)	0.6327(-2),0.5373(-1)
126	0.5261(-2),0.4754(-1)	0.5241(-2),0.4764(-1)
144	0.4627(-2),0.4370(-1)	0.4609(-2),0.4379(-1)
162	0.4294(-2),0.4158(-1)	0.4277(-2),0.4166(-1)
180	0.4189(-2),0.4090(-1)	0.4173(-2),0.4098(-1)
	$500eV$	
18	0.3234(-1),0.1739(0)	0.3174(-1),0.1739(0)
36	0.1929(-1),0.1063(0)	0.1967(-1),0.1070(0)
54	0.1153(-1),0.7883(-1)	0.1151(-1),0.7914(-1)
72	0.7457(-2),0.6105(-1)	0.7428(-2),0.6120(-1)
90	0.5290(-2),0.4940(-1)	0.5273(-2),0.4951(-1)
108	0.4075(-2),0.4178(-1)	0.4060(-2),0.4186(-1)
126	0.3367(-2),0.3681(-1)	0.3351(-2),0.3689(-1)
144	0.2956(-2),0.3371(-1)	0.2941(-2),0.3378(-1)
162	0.2740(-2),0.3201(-1)	0.2727(-2),0.3206(-1)
180	0.2673(-2),0.3146(-1)	0.2659(-2),0.3152(-1)

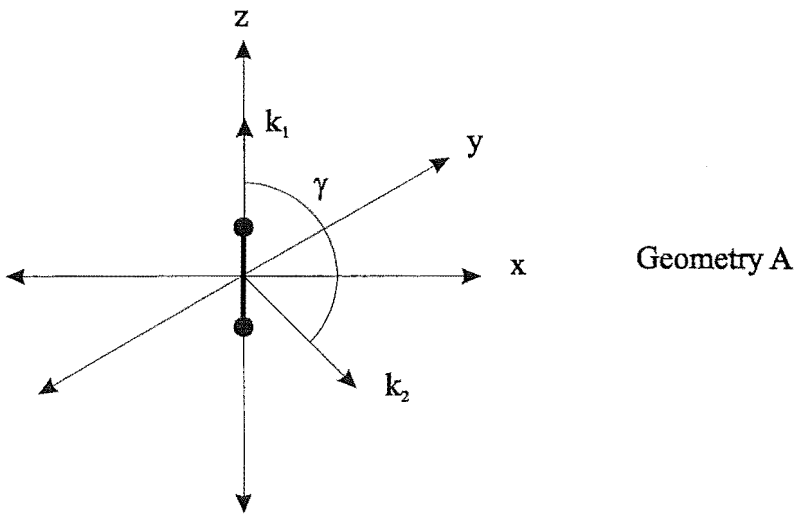


Figure 7-4: H_2 geometry A

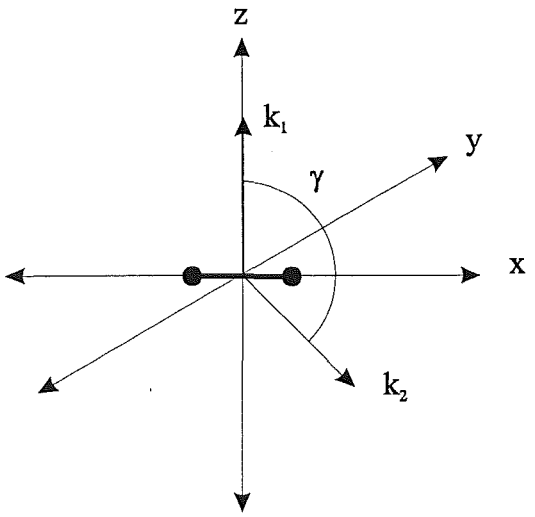
Angular Integrals

Tables 7.14, 7.15 and 7.16 give the imaginary part of the second Born matrix elements at $200eV$ and $500eV$, calculated using the closure approximation, for varying numbers of quadrature points in the integrations. The three scattering geometries are from figures 7-4, 7-5 and 7-6. The closure energy used was $\Delta = 1.3a.u.$ which is the same as that used in the helium calculations.

Comparing the convergence results for the hydrogen integrals with those of helium, the molecular integrals are far slower to converge both in the θ and ϕ coordinates. The scattering geometry has some influence in the rate of convergence, with geometry A having better characteristics than the other two. For geometries B and C, the ϕ coordinate appears to be the more problematic of the two. In a number of cases, even the 64×64 angular grid fails to give convergence to greater than 1%. Numerical integration, using larger quadrature grids begins to become prohibitively expensive, especially when the radial integrations are included.

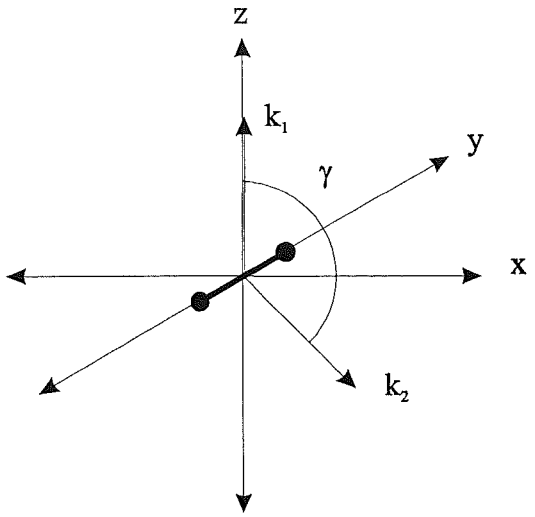
Radial Integrals

Tables 7.17, 7.18 and 7.19 give the real part of the second Born matrix elements at $200eV$ and $500eV$, as for section 7.3.4. In the majority of cases, the radial integrals have achieved



Geometry B

Figure 7-5: H_2 geometry B



Geometry C

Figure 7-6: H_2 geometry C

Table 7.14: Imaginary part of the second Born amplitude calculated using the closure approximation, scattering geometry A

			$200eV, \gamma = 10\,\text{deg}$		
			N		
M	12	16	24	32	48
12	0.7768(0)	0.7768(0)	0.7768(0)	0.7768(0)	0.7768(0)
16	0.7464(0)	0.7464(0)	0.7464(0)	0.7464(0)	0.7464(0)
24	0.7586(0)	0.7586(0)	0.7586(0)	0.7586(0)	0.7586(0)
32	0.7597(0)	0.7597(0)	0.7597(0)	0.7597(0)	0.7597(0)
48	0.7599(0)	0.7599(0)	0.7599(0)	0.7599(0)	0.7599(0)
			$\gamma = 90\,\text{deg}$		
12	0.7714(-1)	0.7707(-1)	0.7707(-1)	0.7707(-1)	0.7707(-1)
16	0.7748(-1)	0.7742(-1)	0.7741(-1)	0.7741(-1)	0.7741(-1)
24	0.7770(-1)	0.7768(-1)	0.7767(-1)	0.7767(-1)	0.7767(-1)
32	0.7773(-1)	0.7773(-1)	0.7772(-1)	0.7772(-1)	0.7772(-1)
48	0.7772(-1)	0.7773(-1)	0.7773(-1)	0.7772(-1)	0.7772(-1)
			$500eV, \gamma = 10\,\text{deg}$		
12	0.4260(0)	0.4260(0)	0.4260(0)	0.4260(0)	0.4260(0)
16	0.3215(0)	0.3213(0)	0.3213(0)	0.3213(0)	0.3213(0)
24	0.3607(0)	0.3607(0)	0.3607(0)	0.3607(0)	0.3607(0)
32	0.3568(0)	0.3568(0)	0.3568(0)	0.3568(0)	0.3568(0)
48	0.3597(0)	0.3597(0)	0.3597(0)	0.3597(0)	0.3597(0)
64	0.3594(0)	0.3594(0)	0.3594(0)	0.3594(0)	0.3594(0)
			$\gamma = 90\,\text{deg}$		
12	-0.1127(-2)	-0.1118(-2)	-0.1119(-2)	-0.1119(-2)	-0.1119(-2)
16	-0.1397(-2)	-0.1389(-2)	-0.1389(-2)	-0.1389(-2)	-0.1389(-2)
24	-0.1759(-2)	-0.1749(-2)	-0.1750(-2)	-0.1751(-2)	-0.1751(-2)
32	-0.1968(-2)	-0.1957(-2)	-0.1957(-2)	-0.1958(-2)	-0.1958(-2)
48	-0.2162(-2)	-0.2150(-2)	-0.2148(-2)	-0.2149(-2)	-0.2149(-2)
64	-0.2227(-2)	-0.2216(-2)	-0.2213(-2)	-0.2214(-2)	-0.2214(-2)

Table 7.15: Imaginary part of the second Born amplitude calculated using the closure approximation, scattering geometry B

			$200eV, \gamma = 10\,\text{deg}$		
			N		
M	16	24	32	48	64
16	0.6430(0)	0.6046(0)	0.6389(0)	0.6327(0)	0.6394(0)
24	0.6469(0)	0.5977(0)	0.6395(0)	0.6304(0)	0.6409(0)
32	0.6472(0)	0.5959(0)	0.6391(0)	0.6294(0)	0.6411(0)
48	0.6472(0)	0.5960(0)	0.6393(0)	0.6293(0)	0.6414(0)
64	0.6472(0)	0.5962(0)	0.6395(0)	0.6293(0)	0.6416(0)
			$\gamma = 90\,\text{deg}$		
16	0.2294(-1)	0.2287(-1)	0.2186(-1)	0.2236(-1)	0.2226(-1)
24	0.2315(-1)	0.2307(-1)	0.2210(-1)	0.2265(-1)	0.2253(-1)
32	0.2320(-1)	0.2311(-1)	0.2218(-1)	0.2271(-1)	0.2260(-1)
48	0.2323(-1)	0.2312(-1)	0.2224(-1)	0.2274(-1)	0.2265(-1)
64	0.2324(-1)	0.2313(-1)	0.2227(-1)	0.2275(-1)	0.2266(-1)
			$500eV, \gamma = 10\,\text{deg}$		
16	0.2178(0)	0.1745(0)	0.2104(0)	0.2005(0)	0.2121(0)
24	0.2226(0)	0.1362(0)	0.1949(0)	0.1795(0)	0.2059(0)
32	0.2231(0)	0.1121(0)	0.1814(0)	0.1686(0)	0.2035(0)
48	0.2232(0)	0.9430(-1)	0.1695(0)	0.1637(0)	0.2043(0)
64	0.2232(0)	0.9054(-1)	0.1663(0)	0.1633(0)	0.2050(0)
			$\gamma = 90\,\text{deg}$		
16	-0.7733(-2)	-0.7622(-2)	-0.8524(-2)	-0.8038(-2)	-0.8138(-2)
24	-0.7531(-2)	-0.7428(-2)	-0.8298(-2)	-0.7761(-2)	-0.7887(-2)
32	-0.7473(-2)	-0.7381(-2)	-0.8183(-2)	-0.7680(-2)	-0.7799(-2)
48	-0.7433(-2)	-0.7356(-2)	-0.8102(-2)	-0.7639(-2)	-0.7739(-2)
64	-0.7421(-2)	-0.7348(-2)	-0.8070(-2)	-0.7630(-2)	-0.7723(-2)

Table 7.16: Imaginary part of the second Born amplitude calculated using the closure approximation, scattering geometry C

			$200eV, \gamma = 10\,\text{deg}$		
			N		
M	16	24	32	48	64
16	0.6608(0)	0.6401(0)	0.6114(0)	0.6434(0)	0.6334(0)
24	0.6671(0)	0.6434(0)	0.6425(0)	0.6580(0)	0.6524(0)
32	0.6672(0)	0.6434(0)	0.6410(0)	0.6581(0)	0.6520(0)
48	0.6672(0)	0.6434(0)	0.6427(0)	0.6584(0)	0.6527(0)
64	0.6672(0)	0.6434(0)	0.6430(0)	0.6584(0)	0.6528(0)
			$\gamma = 90\,\text{deg}$		
16	0.7716(-1)	0.7685(-1)	0.7772(-1)	0.7732(-1)	0.7741(-1)
24	0.7743(-1)	0.7716(-1)	0.7800(-1)	0.7755(-1)	0.7767(-1)
32	0.7750(-1)	0.7723(-1)	0.7804(-1)	0.7761(-1)	0.7771(-1)
48	0.7752(-1)	0.7725(-1)	0.7803(-1)	0.7762(-1)	0.7771(-1)
64	0.7753(-1)	0.7725(-1)	0.7801(-1)	0.7762(-1)	0.7770(-1)
			$500eV, \gamma = 10\,\text{deg}$		
16	0.2530(0)	0.2350(0)	0.1323(0)	0.2312(0)	0.1987(0)
24	0.2571(0)	0.2367(0)	0.1949(0)	0.2476(0)	0.2292(0)
32	0.2574(0)	0.2369(0)	0.1748(0)	0.2484(0)	0.2240(0)
48	0.2575(0)	0.2369(0)	0.1878(0)	0.2491(0)	0.2286(0)
64	0.2574(0)	0.2369(0)	0.1900(0)	0.2491(0)	0.2291(0)
			$\gamma = 90\,\text{deg}$		
16	-0.1354(-2)	-0.1372(-2)	-0.1403(-2)	-0.1387(-2)	-0.1389(-2)
24	-0.1723(-2)	-0.1744(-2)	-0.1753(-2)	-0.1752(-2)	-0.1751(-2)
32	-0.1935(-2)	-0.1956(-2)	-0.1953(-2)	-0.1963(-2)	-0.1959(-2)
48	-0.2129(-2)	-0.2150(-2)	-0.2141(-2)	-0.2157(-2)	-0.2153(-2)
64	-0.2193(-2)	-0.2215(-2)	-0.2208(-2)	-0.2221(-2)	-0.2218(-2)

Table 7.17: Real part of the H_2, second Born matrix elements as a function of the number of radial quadrature points (scattering geometry A)

$200eV, \gamma = 10\,\text{deg}$	
M	$\text{Re}(f^{(1)})$
12	0.4174(0)
16	0.4249(0)
24	0.4259(0)
32	0.4263(0)
48	0.4269(0)
	$\gamma = 90\,\text{deg}$
12	0.4418(-2)
16	0.4895(-2)
24	0.4424(-2)
32	0.4459(-2)
48	0.4391(-2)
$500eV, \gamma = 10\,\text{deg}$	
12	0.1095(0)
16	0.1086(0)
24	0.1139(0)
32	0.1129(0)
48	0.1126(0)
	$\gamma = 90\,\text{deg}$
12	0.1551(-1)
16	0.1583(-1)
24	0.1564(-1)
32	0.1568(-1)
48	0.1573(-1)

satisfactory convergence at $M = 48$ or less.

From the results of the helium calculations, it is clear the numerical techniques applied to the integrals required in the evaluation of the second Born matrix elements via the closure approximation are converging to the correct values. In the atomic case the convergence is sufficiently rapid for this method to be considered a viable method of calculation of the desired integrals. Applying the same techniques to molecular hydrogen, the resulting rate of convergence in the angular components is drastically reduced. Even using extensive angular grids fails to produce satisfactory results. Table 7.20 gives the numerical results for the $200eV, \gamma = 10\,\text{deg}$ integration for geometry B, with N extended to 128, and shows the integrals eventually converge. Angular grids greater than 64×64, become prohibitively expensive to calculate, due to the excessive amount of computation required.

Table 7.18: Real part of the H_2, second Born matrix elements as a function of the number of radial quadrature points, (scattering geometry B)

$200eV, \gamma = 10\,\text{deg}$	
M	$\text{Re}(f^{(1)})$
12	0.1779(0)
16	0.1811(0)
24	0.1809(0)
32	0.1807(0)
48	0.1807(0)
	$\gamma = 90\,\text{deg}$
12	-0.6060(-1)
16	-0.5939(-1)
24	-0.5986(-1)
32	-0.6002(-1)
48	-0.5995(-1)
$500eV, \gamma = 10\,\text{deg}$	
12	0.4685(-2)
16	0.4722(-2)
24	0.5103(-2)
32	0.5475(-2)
48	0.5435(-2)
	$\gamma = 90\,\text{deg}$
12	-0.1454(-1)
16	-0.1427(-1)
24	-0.1442(-1)
32	-0.1412(-1)
48	-0.1417(-1)

Table 7.19: Real part of the H_2, second Born matrix elements as a function of the number of radial quadrature points, (scattering geometry C)

$200eV, \gamma = 10\,\text{deg}$	
M	$\text{Re}(f^{(1)})$
12	0.1949(0)
16	0.1986(0)
24	0.1986(0)
32	0.1984(0)
48	0.1984(0)
	$\gamma = 90\,\text{deg}$
12	0.4287(-2)
16	0.4783(-2)
24	0.4352(-2)
32	0.4390(-2)
48	0.4305(-2)
$500eV, \gamma = 10\,\text{deg}$	
12	0.1861(-1)
16	0.1899(-1)
24	0.1974(-1)
32	0.2023(-1)
48	0.2024(-1)
	$\gamma = 90\,\text{deg}$
12	0.1556(-1)
16	0.1588(-1)
24	0.1570(-1)
32	0.1574(-1)
48	0.1579(-1)

Table 7.20: Imaginary part of the second Born amplitude as a function of the number of quadrature points in the ϕ coordinate ($M = 48, 200eV, \gamma = 10\,\text{deg}$, geometry B)

		N		
48	64	72	96	128
0.6293(0)	0.6414(0)	0.6387(0)	0.6399(0)	0.6397(0)

Numerical integration as described above, is not a feasible method for the evaluation of the second Born matrix elements for molecular targets. There are two obvious places where these techniques could be made more efficient. Firstly, it is critical to evaluate the first Born amplitudes as efficiently as possible because they are so extensively called, when calculating the integrand of the integrals to be evaluated. Secondly, studying the individual terms in the second Born amplitudes it is evident, the closure integrals I_c, are the terms which have the most trouble converging. Thus any scheme which reduces the computational requirement for these integrals, would be of most benefit in the calculation of the full second Born terms. It is envisaged that drastic changes to the computational techniques described are required, before any approach based on these ideas can be considered viable in the calculation of molecular second Born amplitudes.

Chapter 8

Possible Future Directions

This chapter outlines various extensions of the work covered in chapters 6 and 7. The work in those chapters is incomplete, and so it was considered important to discuss how it may be extended. It is proposed that for intermediate energy scattering, a closure approximation to the second Born like matrix elements required in the evaluation of the Schwinger variational method can be used. The intermediate energies range from above the first ionization threshold of the target, to energies where perturbation theory can be reliably applied, usually taken as around $150eV$. In this energy region, the number of discrete open channels becomes large and the continuum channels must also be included in the Green's function to give a reasonable approximation to the matrix elements.

The second Born approximation, applied to molecular scattering as formulated in chapter 7.3, does not produce a viable numerical method for calculating scattering data. One possibility for calculating these terms is to use single center expansions and partial wave analysis. This reduces the three dimensional integral over $\mathbf{k}$ to a one dimensional integral over $|\mathbf{k}|$ at the expense of introducing an infinite sum over the partial wave amplitudes. At higher energies a large number of these partial wave amplitudes contribute to the scattering amplitude, thus making an approach based on partial waves more computationally demanding at higher energies.

8.1 The Closure Approximation and Schwinger's Variational Principle

Evaluation of the Schwinger functionals, eqns 5.5 and 5.8 requires the calculation of the second Born like matrix elements

$$\langle \phi^{(-)}_{\mathbf{k_1},n'} | V G_0^+ V | \phi^{(+)}_{\mathbf{k_2},n} \rangle = \lim_{\eta \to 0+} \sum_i \int d\mathbf{k} \frac{\langle \phi^{(-)}_{\mathbf{k_1},n'} | V | \psi_i \phi_{\mathbf{k}} \rangle \langle \psi_i \phi_{\mathbf{k}} | V | \phi^{(+)}_{\mathbf{k_2},n} \rangle}{k^2 - k_i^2 - i\eta}. \tag{8.1}$$

The operator G_0^+ is the two particle, multichannel Green's operator (see eqn 5.40). Applications of the Schwinger variational principle to atomic scattering have used a number of ways to estimate these matrix elements. The original work of McKoy *et al.* [23, 26] for elastic scattering of very low energy electrons, included only the ground state in the summation over the intermediate states. This is simply the Schwinger variational principle applied to potential scattering from the target ground state. This is the method used in section 6.3.1. McKoy and Takatsuka developed the *multichannel T-matrix theory* [33, 34] which includes a finite set of intermediate states. This approach uses an open channel projected Green's operator and adds back the contribution from the closed channels, approximated using pseudostates. This approximation has been applied to a number of systems at low energy but becomes unstable at higher energies [52], as more open channels are included in the calculation of the Green's function. It also assumes the ionization channels are closed. Plummer *et al.* [52] has studied the intermediate energy scattering of electrons from atomic hydrogen using the Schwinger variational principle, approximating the second Born like terms by a pseudostate expansion, and applying the T-matrix averaging technique of Burke *et al.* [53] to the resulting transition amplitudes.

It is possible to apply the closure approximation to eqn 8.1, which gives an alternative method of estimation of these terms when using the Schwinger variational principle. This could be useful either in itself, as a method of applying Schwinger's variational principle or, as a method of optimizing the pseudostate basis to be used in a subsequent calculation. It would be most useful at intermediate energies ($10eV < E < 100eV$) where it is important to include the contribution from the continuum in the calculation of the Green's function. The

closure approximation, through the closure integral, gives some weight to all intermediate states including the continuum states at the expense of having to average the energy spectrum.

Pseudostate expansions [104, 105, 106] use a finite set of states to expand the Green's function. The states used are not necessarily eigenfunctions of the target Hamiltonian but do diagonalize it. This approach approximates the infinite set of intermediate states by a finite set of states, but does treat the energy differences exactly. Generally, one or more of the states are chosen to have an energy in the continuum. This approach has been used in the Schwinger variational principle, the second Born approximation and close coupling calculations. One of the difficulties in using pseudostate expansions is determining the appropriate pseudostate basis. A method of optimizing a given basis has been discussed by Walters [57]. It consists of firstly calculating the matrix elements of the Green's function using the closure approximation with some suitably chosen closure energy Δ. The calculation is repeated using the proposed pseudostate basis, and the basis adjusted until the two matrix elements agree within some chosen limits. Finally, the matrix elements are calculated with the corrected pseudostate basis, using the true energy differences.

Following section 5.3.1, the closure approximation applied to eqn 8.1 can be written

$$\lim_{\eta\to 0^+} \sum_i \int d\mathbf{k} \frac{\langle \phi^{(-)}_{\mathbf{k_1},n'} | V | \psi_i \phi_{\mathbf{k}} \rangle \langle \psi_i \phi_{\mathbf{k}} | V | \phi^{(+)}_{\mathbf{k_2},n} \rangle}{k^2 - k_i^2 - i\eta} \approx$$
$$\sum_{i=1}^{N} \left[I_b(n,n';i,k_i) - I_b(n,n';i,\bar{k}) \right] + I_c(n,n';\bar{k}) \tag{8.2}$$

where

$$I_b(n,n';i,z) = \lim_{\eta\to 0^+} \int d\mathbf{k} \frac{\langle \phi^{(-)}_{\mathbf{k_1},n'} | V | \psi_i \phi_{\mathbf{k}} \rangle \langle \psi_i \phi_{\mathbf{k}} | V | \phi^{(+)}_{\mathbf{k_2},n} \rangle}{k^2 - z^2 - i\eta} \tag{8.3}$$

and

$$I_c(n,n';\bar{k}) = \sum_{allstates} \lim_{\eta\to 0^+} \int d\mathbf{k} \frac{\langle \phi^{(-)}_{\mathbf{k_1},n'}|V|\psi_i\phi_\mathbf{k}\rangle\langle\psi_i\phi_\mathbf{k}|V|\phi^{(+)}_{\mathbf{k_2},n}\rangle}{k^2-\bar{k}^2-i\eta}$$
$$= \lim_{\eta\to 0^+} \int d\mathbf{k} \frac{\langle \phi^{(-)}_{\mathbf{k_1},n'}|V|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|V|\phi^{(+)}_{\mathbf{k_2},n}\rangle}{k^2-\bar{k}^2-i\eta}. \tag{8.4}$$

Considering only direct scattering events and requiring the scattering states $\phi^{(\pm)}_{\mathbf{k},n}$ to be the antisymmetrised product of N target orbitals and a scattering orbital $\phi_s(\mathbf{r_a})$, the matrix elements

$$\langle \phi^{(-)}_{\mathbf{k_1},n'}|V|\psi_i\phi_\mathbf{k}\rangle \qquad \langle\psi_i\phi_\mathbf{k}|V|\phi^{(+)}_{\mathbf{k_2},n}\rangle \tag{8.5}$$

can be written

$$\langle\psi_{n'}|\langle\phi_{s'}(\mathbf{r_a})|V|\phi_\mathbf{k}(\mathbf{r_a})\rangle|\psi_i\rangle \qquad \langle\psi_i|\langle\phi_\mathbf{k}(\mathbf{r_a})|V|\phi_s(\mathbf{r_a})\rangle|\psi_n\rangle \tag{8.6}$$

respectively.

Using these in eqn 8.2 leads to expressions the for I_b and I_c,

$$I_b(n,n';i,z) = \lim_{\eta\to 0^+} \int d\mathbf{k} \frac{\langle\psi_{n'}|\langle\phi_{s'}|V|\phi_\mathbf{k}\rangle|\psi_i\rangle\langle\psi_i|\langle\phi_\mathbf{k}|V|\phi_s\rangle|\psi_n\rangle}{k^2-z^2-i\eta} \tag{8.7}$$

and

$$I_c(n,n';\bar{k}) = \lim_{\eta\to 0^+} \int d\mathbf{k} \frac{\langle\psi_{n'}|\langle\phi_{s'}|V|\phi_\mathbf{k}\rangle\langle\phi_\mathbf{k}|V|\phi_s\rangle|\psi_n\rangle}{k^2-\bar{k}^2-i\eta}. \tag{8.8}$$

Considering the I_b terms initially, a method for calculating these integrals has been given in section 6.3.1. The bound-free matrix elements of the interaction potential, for atomic orbitals expanded in Gaussian functions, can be written in the form,

$$\lim_{\eta\to 0^+} \int d\mathbf{k} \frac{\langle\psi_{n'}|\langle\phi_{s'}|V|\phi_\mathbf{k}\rangle|\psi_i\rangle\langle\psi_i|\langle\phi_\mathbf{k}|V|\phi_s\rangle|\psi_n\rangle}{k^2-k_i^2-i\eta} = \lim_{\eta\to 0^+} \int d\mathbf{k} \frac{A(k)}{k^2-k_i^2-i\eta} B(\hat{\mathbf{k}}) \tag{8.9}$$

where $B(\hat{\mathbf{k}})$ is a simple function of the angular component of the vector $\mathbf{k}$. This allows the

angular integral of $\mathbf{k}$ in eqn 8.7 to be completed analytically, leaving a principle value, radial integral to be estimated numerically.

The second integral required of the calculation of eqn 8.2 is the closure integral, given by

$$I_c(n,n';\bar{k}) = \lim_{\eta\to 0^+}\int d\mathbf{k}\frac{\langle\psi_{n'}|\langle\phi_{s'}|V|\phi_{\mathbf{k}}\rangle\langle\phi_{\mathbf{k}}|V|\phi_s\rangle|\psi_n\rangle}{k^2-\bar{k}^2-i\eta}. \tag{8.10}$$

Using elastic scattering from the ground state of helium as an example, the numerator can be written

$$\begin{aligned}&\langle\psi_0|\langle\phi_{s'}|V|\phi_{\mathbf{k}}\rangle\langle\phi_{\mathbf{k}}|V|\phi_s\rangle|\psi_0\rangle = \\ &\int d\tau_1\int d\tau_2\psi_0^*(\mathbf{r_1},\mathbf{r_2})\left(\left(\int d\tau_a\phi_{s'}^*(\mathbf{r_a})(-2/r_a+1/r_{1a}+1/r_{2a})\phi_{\mathbf{k}}(\mathbf{r_a})\right)\right. \\ &\left.\left(\int d\tau_a\phi_{\mathbf{k}}^*(\mathbf{r_a})(-2/r_a+1/r_{1a}+1/r_{2a})\phi_s(\mathbf{r_a})\right)\right)\psi_0(\mathbf{r_1},\mathbf{r_2})\end{aligned} \tag{8.11}$$

Using eqn 6.8 for the helium ground state, and expanding gives

$$\begin{aligned}&\langle\psi_0|\langle\phi_{s'}|V|\phi_{\mathbf{k}}\rangle\langle\phi_{\mathbf{k}}|V|\phi_s\rangle|\psi_0\rangle = \\ &2\left[\left\langle\phi_{s'}\left|-\frac{2}{r_a}\right|\phi_{\mathbf{k}}\right\rangle\left\langle\phi_{\mathbf{k}}\left|-\frac{2}{r_a}\right|\phi_s\right\rangle+2\left\langle\phi_{s'}\left|-\frac{2}{r_a}\right|\phi_{\mathbf{k}}\right\rangle\left\langle\phi_{\mathbf{k}}\phi_{1s}^{\mathrm{He}}\left|\frac{1}{r_{1a}}\right|\phi_s\phi_{1s}^{\mathrm{He}}\right\rangle\right. \\ &+2\left\langle\phi_{\mathbf{k}}\left|-\frac{2}{r_a}\right|\phi_s\right\rangle\left\langle\phi_{s'}\phi_{1s}^{\mathrm{He}}\left|\frac{1}{r_{1a}}\right|\phi_{\mathbf{k}}\phi_{1s}^{\mathrm{He}}\right\rangle+\left\langle\phi_{s'}\phi_{1s}^{\mathrm{He}}\left|\frac{1}{r_{1a}}\right|\phi_{\mathbf{k}}\phi_{1s}^{\mathrm{He}}\right\rangle\left\langle\phi_{\mathbf{k}}\phi_{1s}^{\mathrm{He}}\left|\frac{1}{r_{2a}}\right|\phi_s\phi_{1s}^{\mathrm{He}}\right\rangle \\ &+\left\langle\phi_{\mathbf{k}}\phi_{1s}^{\mathrm{He}}\left|\frac{1}{r_{1a}}\right|\phi_s\phi_{1s}^{\mathrm{He}}\right\rangle\left\langle\phi_{s'}\phi_{1s}^{\mathrm{He}}\left|\frac{1}{r_{2a}}\right|\phi_{\mathbf{k}}\phi_{1s}^{\mathrm{He}}\right\rangle \\ &\left.+2\left\langle\phi_{1s}^{\mathrm{He}}\left|\left\langle\phi_{s'}\left|\frac{1}{r_{1a}}\right|\phi_{\mathbf{k}}\right\rangle\left\langle\phi_{\mathbf{k}}\left|\frac{1}{r_{1a}}\right|\phi_s\right\rangle\right|\phi_{1s}^{\mathrm{He}}\right\rangle\right]\end{aligned} \tag{8.12}$$

All the terms in this expression except for the final one, are found in the calculation of I_b. The final integration over $\mathbf{k}$ for these terms proceeds as for the I_b integral.

The final term is

$$\lim_{\eta\to 0^+}\int\frac{d\mathbf{k}}{k^2-\bar{k}^2-i\eta}\left\langle\phi_{1s}^{\mathrm{He}}\left|\left\langle\phi_{s'}\left|\frac{1}{r_{1a}}\right|\phi_{\mathbf{k}}\right\rangle\left\langle\phi_{\mathbf{k}}\left|\frac{1}{r_{1a}}\right|\phi_s\right\rangle\right|\phi_{1s}^{\mathrm{He}}\right\rangle. \tag{8.13}$$

The two inner matrix elements can be completed, for orbitals expanded in s-Gaussian func-

tions they can be written

$$\left\langle \phi_{s'} \left| \frac{1}{r_{1a}} \right| \phi_{\mathbf{k}} \right\rangle = \left\langle \phi_{\mathbf{k}} \left| \frac{1}{r_{1a}} \right| \phi_{s} \right\rangle = F(k, r_1) \tag{8.14}$$

were $F(k, r_1)$ is a function only of the magnitudes of the vectors $\mathbf{k}$ and $\mathbf{r_1}$. Substituting back into eqn 8.13, the angular integrals over $\mathbf{k}$ and $\mathbf{r_1}$ can be completed leaving a final two dimensional radial integral. The integrand for the final integrals is a complicated expression involving the error function with complex arguments and the $1/(k^2 - \bar{k}^2)$ factor from the $\mathbf{k}$ integral. This must be estimated numerically.

It is quite feasible to apply the closure approximation to the evaluation of the matrix elements of eqn 8.1 for helium, for the simple case of all orbitals being expanded in s-Gaussian functions. Higher order orbitals complicate the equations but, the angular integrals are still able to be completed analytically, so it should still be possible to calculate all the terms required. This approach could be immediately be applied to electron scattering from helium to determine the feasibility of the calculations. At lower energies there is sufficient data from other computational methods to determine whether using the closure approximation gives any improvement over existing theories.

8.2 Single Center Expansions, Partial Wave Expansions and Molecular Orientation

8.2.1 Single Center Expansions

For molecular scattering, where the target orbitals are expanded in functions centered on the nuclei, the integrals required for the evaluation of scattering data become multicenter. In a number of cases, the solution of these integrals remain analytic, but considerably complicate the resulting equations.

Lucchese and coworkers [21] have developed methods for defining molecular orbitals, interaction potentials and the free particle Green's function in single center expansions, which allows the well developed numerical techniques of atomic physics to be applied to molecular systems.

The single center expansion of the general function $f(\theta, \phi, r)$, is written

$$f(\theta,\phi,r) = \sum_{LM} \frac{1}{r} f_{LM}(r) Y_{LM}(\hat{\mathbf{r}}) \tag{8.15}$$

where

$$f_{LM}(r) = r \int d\hat{\mathbf{r}} f(\theta,\phi,r) Y_{LM}(\hat{\mathbf{r}}). \tag{8.16}$$

The property which makes single center expansions useful, is the fact that the overlap integral between two functions of the form of eqn 8.15 reduces to the sum of the radial integrals,

$$\int d\mathbf{r}\, f^*(\theta,\phi,r) g(\theta,\phi,r) = \sum_{LM} \int_0^\infty dr\, f^*_{LM}(r) g_{LM}(r). \tag{8.17}$$

Single center expansions of Slater [107], Cartesian Gaussian [25] and spherical Gaussian functions [21] have been reported.

The $1/|\mathbf{r_1} - \mathbf{r_2}|$ term present in the interaction potential can also be expanded in spherical harmonics [108],

$$\frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} = 4\pi \sum_{LM} \frac{1}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y^*_{LM}(\hat{\mathbf{r}}_1) Y_{LM}(\hat{\mathbf{r}}_2) \tag{8.18}$$

where $r_<$ and $r_>$ are the lesser and greater respectively, of r_1 and r_2.

Faisal [109] use these expansions to develop a multipole expansion of the static potential, produced by a linear molecule expanded in functions centered on the nuclei. Burke and Sinfailam [110] extended this work to include exchange. Using molecular interaction potentials, expanded about a single center, reduces the required calculation to that of scattering from a pseudo atom. This is at the expense of having to include a possibly large number of multipoles to adequately describe the molecular potential. Also for molecular scattering, the target has a fixed orientation with respect to the asymptotic momentum vectors. For atomic systems, the quantization axis can have any orientation, and is usually chosen along the incident electron's momentum vector or the momentum change vector of the scattered electron, depending on the detail of the calculation.

A single center expansion of the principle part of the free particle Green's function has also been reported by Lucchese and McKoy [21].

8.2.2 Partial Wave Expansions

The stationary, free wave states $|\Phi_{\mathbf{k}}\rangle$ from section 3.1 (see eqns 3.2 and 3.3) can also be expanded in the basis of angular momentum states, written $|Elm\rangle$. The states $|Elm\rangle$ are eigenstates of the free particle wave equation, written in spherical polar coordinates, and

$$\langle \mathbf{r}|Elm\rangle = i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{r}}), \tag{8.19}$$

$$|\phi_{\mathbf{k}}\rangle = \sum_{lm} |Elm\rangle Y_{lm}(\hat{\mathbf{k}}). \tag{8.20}$$

The importance of the angular momentum basis for atomic systems is that, because the scattering operator commutes with the L^2 and L_z operators, the matrix elements of the scattering operator are diagonal in this basis, i.e.

$$\langle Elm|S|E'l'm'\rangle = \delta(E - E')\delta_{ll'}\delta_{mm'} s_l(E), \tag{8.21}$$

(It can be shown that the terms $s_l(E)$ are independent of m)

The stationary scattering states can also be defined in terms of partial waves, through the partial wave Lippmann-Schwinger equation,

$$|\phi^{(\pm)}_{Elm}\rangle = |Elm\rangle + G^{\pm}_0(E)V|\phi^{(\pm)}_{Elm}\rangle. \tag{8.22}$$

For molecular scattering, the angular momentum basis is useful because it simplifies the integral over the orientation of the target with respect to the reference frame defined by the asymptotic vectors $\mathbf{k_1}$ and $\mathbf{k_2}$. (see section 8.2.3)

Expressions for the partial wave, first Born scattering amplitudes for electron H_2 scattering in the static exchange approximation have been reported by Fliflet and McKoy [25], using the single center expansions of the static and exchange potential given by Faisal and Burke and Sinfailam respectively. The static, partial wave first Born scattering amplitudes can be used to calculate the second Born matrix elements, using the fact that the spectral representation of the two particle Green's function can be written in a basis of angular momentum states. The I_b terms can be written as the sum of partial wave $I_b(lm)$ terms,

$$
\begin{aligned}
I_b &= \int d\mathbf{k} \frac{\langle \phi_{\mathbf{k}_1} | V | \phi_{\mathbf{k}} \rangle \langle \phi_{\mathbf{k}} | V | \phi_{\mathbf{k}_2} \rangle}{k^2 - \bar{k}^2} \\
&= \sum_{lm} I_b(lm) Y^*_{lm}(\hat{\mathbf{k}_1}) Y_{lm}(\hat{\mathbf{k}_2})
\end{aligned} \tag{8.23}
$$

where

$$
I_b(lm) = \sum_{l'm'} \int dk \frac{\langle E_{k_1} lm | V | E_k l'm' \rangle \langle E_k l'm' | V | E_{k_2} lm \rangle}{k^2 - \bar{k}^2}. \tag{8.24}
$$

and the interaction potential V is assumed to be the static potential of the atomic or molecular target (see section 4.5).

The I_b terms can thus be reduced to a sum over l and m, of the principle value radial integrals over k. The closure integral I_c can again be expanded in partial waves, by using the single center expansion of the potential and the molecular orbitals. The Schwinger variational principle can also be formulated in terms of partial waves [25, 23, 28, 26, 27, 29, 35, 36, 41]. These ideas can also be applied to the closure integral in section 8.1.

8.2.3 Nuclear Motion and the Adiabatic Nuclei Approximation

All discussion in this thesis to date, has assumed that the nuclei of the target atom or molecule remains fixed throughout the whole scattering event. This assumption is known as the *adiabatic nuclei approximation* [12, 111, 112, 113, 114]. Considering an intuitive semi-classical picture of an electron-molecule scattering event, when the incident electron is close to the target, the interaction potential dominates the motion of the free electron. That is, the electron and the target have coupled strongly, with the angular momentum of the system being described by the quantum numbers J and M_J, which are the quantum numbers for the total system of electron plus molecule. For a system of this nature, it is sensible to formulate the theoretical description of the system in the coordinate frame of the molecule. The Born-Oppenheimer approximation can be used, so the theoretical treatment becomes the positive energy equivalent of typical bound state molecular calculations. The nuclear motion can be considered subsequent to the treatment of the electronic motions as is the case with bound state calculations.

When the free electron moves sufficiently far away from the molecule, the interaction potential becomes relatively less important, and the motions of the nuclei can become important. In this region, the angular momentum quantum numbers of the free molecule become good quantum numbers and the system can be described as a positive energy electron moving in the field of a freely rotating and vibrating molecule. This system is best formulated in the fixed laboratory reference frame, typically with the z axis taken along the free electron's, incident momentum vector. There is thus, a boundary between the inner region, where the total system is described in the molecular reference frame, and the outer region where system consists of an electron plus rotating and vibrating molecule, described in the fixed laboratory reference frame. The so called *frame transformation methods* [115, 116, 11] determine solutions of the scattering equations in the inner region in the molecular frame, then at a chosen boundary, the solutions are transformed into the laboratory frame, the nuclear Hamiltonian is introduced and the solutions continued into the asymptotic region where scattering information can be derived. The adiabatic nuclei approximation is equivalent to assuming that the boundary in the frame transformation methods, can be moved out to infinity. It is valid when the time required for the free electron to traverse the interaction potential is short, with respect to the rotational and vibrational periods of the molecule.

To account for motion of the target nuclei, the approximation of Chase [117] is invoked. For diatomic targets, the initial and final target nuclear states are written $|\chi_{\nu_0 j_0}\mathbf{R}\rangle$ and $|\chi_{\nu_n j_n}\mathbf{R}\rangle$ respectively, where the quantum number ν and j represent the vibrational quantum number and j represents the rotational quantum numbers. The vector $\mathbf{R}$ is the internuclear vector in the laboratory frame. Now, the scattering amplitude for the transition from the state $|\chi_{\nu_0 j_0}\mathbf{R}\rangle$ to $|\chi_{\nu_n j_n}\mathbf{R}\rangle$ is given by

$$f^L(\mathbf{k_2}n\nu_n j_n \rightarrow \mathbf{k_1}0\nu_0 j_0) = \langle \chi_{\nu_n j_n}\mathbf{R}|f_L(\mathbf{k_2}n \rightarrow \mathbf{k_1}0;\hat{\mathbf{R}})|\chi_{\nu_0 j_0}\mathbf{R}\rangle \tag{8.25}$$

where $f^L(\mathbf{k_2}n \rightarrow \mathbf{k_1}0;\hat{\mathbf{R}})$ is the fixed nuclei scattering amplitude for the transition from the electronic state 0 to the state n, defined in the laboratory reference frame, with the z axis lying along the vector $\mathbf{k_1}$. The vector $\hat{\mathbf{R}}$ denotes the orientation of the internuclear axis with respect to the laboratory reference frame. (For non-linear targets, the orientation of the molecule with respect to the laboratory frame is defined by the three *Euler angles*)

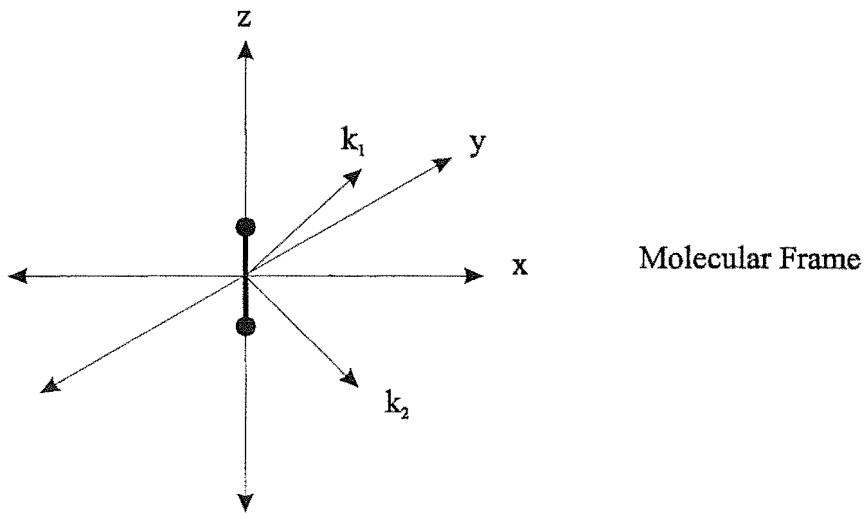


Figure 8-1: Scattering geometry in the center of mass coordinate frame

Considering only the rotational motion of the target, if the rotational energies are assumed degenerate, the rotationally averaged differential cross section is simply the integral over all target orientations, of the square of the amplitude $f^L(\mathbf{k_2}n \rightarrow \mathbf{k_1}0;\hat{\mathbf{R}})$,

$$\frac{d\sigma}{d\Omega}(\mathbf{k_2}n \rightarrow \mathbf{k_1}0) = \frac{k_2}{k_1}\int d\hat{\mathbf{R}} \left| f^L(\mathbf{k_2}n \rightarrow \mathbf{k_1}0;\hat{\mathbf{R}}) \right|^2 . \tag{8.26}$$

The steps involved in calculating the differential cross section, using the adiabatic nuclei approximation, in terms of the molecular frame partial wave scattering amplitudes is briefly outlined. This is specific to linear targets, although the concepts can be extended to non-linear targets.

1. The molecular frame partial wave amplitudes are determined from the partial wave transition matrix elements, via a suitable approximation. The molecular frame scattering amplitude (see fig 8-1) can be expanded in the partial wave amplitudes,

$$f^M(\mathbf{k_2}n \rightarrow \mathbf{k_1}0) = 4\pi \sum_{ll'mm'} f^L_{ll'mm'}(\mathbf{k_2}n \rightarrow \mathbf{k_1}0) Y_{lm}(\hat{\mathbf{k}}_2) Y^*_{l'm'}(\hat{\mathbf{k}}_1). \tag{8.27}$$

2. The lab frame scattering amplitude (see fig 8-2) is expanded in terms of the partial

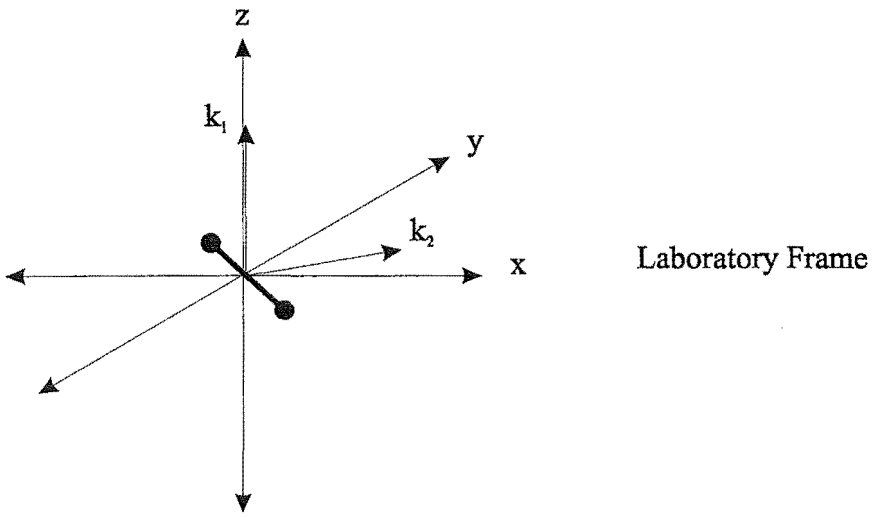


Figure 8-2: Scattering geometry in the laboratory coordinate frame

wave, molecular frame amplitudes, after a suitable rotation is performed, using rotational harmonics [118] and the properties of the spherical harmonics,

$$f^L(\mathbf{k_2}n \rightarrow \mathbf{k_1}0;\hat{\mathbf{R}}) = \sum_{ll'mm',m''} a_{ll'mm'} f^M_{ll'mm'}(\mathbf{k_2}, n \rightarrow \mathbf{k_1}0) D^{(l')*}_{m''m}(\hat{\mathbf{R}}) D^{(l')}_{0m}(\hat{\mathbf{R}}) Y_{lm''}(\hat{\mathbf{k}}_2). \tag{8.28}$$

3. Expression 8.28 is substituted into eqn 8.26 giving

$$\frac{d\sigma}{d\Omega}(\mathbf{k_2}n \rightarrow \mathbf{k_1}0) = \frac{k_2}{k_1} \sum_L A_L P_L(\theta) \tag{8.29}$$

where $P_L(\theta)$ is the L^{th} order Legendre polynomial whose argument is the scattering angle, and

$$A_L = \frac{1}{4\pi} \sum_{ll'mm'} \sum_{\lambda\lambda'\mu\mu'} a_{ll'mm'} f^M_{ll'mm'} a_{\lambda\lambda'\mu\mu'} f^M_{\lambda\lambda'\mu\mu'} C(ll'mm';\lambda\lambda'\mu\mu';L) \tag{8.30}$$

where C is a combination of Clebsch-Gordon coefficients [119]

Calculation of the molecular frame partial wave amplitudes, via a suitable approximation, thus reduces the final integral required over the molecular orientation, to a summation of the partial wave amplitudes.

Seigel, Dill and Dehmer [120], give an alternative method of completing the final summation over the partial waves, eqn 8.29. Their formulation is in terms of the angular momentum transferred from the electron to the target, and exploits the rapid falloff in scattering with increasing angular momentum transfer.

It is quite feasible to express the first and second Born scattering amplitudes and the Schwinger variational principle in terms of partial wave expansions. This is true also, of the formulas for the closure approximation to the matrix elements of the Green's functions for the Schwinger and second Born approximations. Because of the difficulty in using the $\exp(i\mathbf{k}\cdot\mathbf{r})$ basis, for the calculation of second Born matrix elements from molecular targets, it would be interesting to compare the computational requirements of calculating these terms using partial wave expansions, bearing in mind that, as the energy of the scattering system increases, the number of partial waves that contribute to the scattering amplitude, also increases. Because the Schwinger variational principle is a low and intermediate energy theory, there are obvious advantages in using a partial wave expansion when studying molecular scattering.

Chapter 9

Conclusions

This chapter gives a summary of the results and conclusions obtained in chapters 6, 7 and 8.

Programs to calculate high energy, electron-helium second Born amplitudes via the simplified second Born approximation of Holt *et al.* [71], have been written. The results obtained have been compared with published results [70, 71, 72] to ensure the numerical techniques used have been correctly applied. The wave functions used to describe the stationary target states in this work were expanded in Slater functions. The use of Gaussian functions to describe the target orbitals was investigated, because of the intention of extending the theoretical treatment to molecular systems. The resulting equations for the second Born matrix elements could not be reduced to any useful form, so the first Born amplitudes were fitted to the corresponding Slater expressions allowing the second Born matrix elements to be calculated. The results obtained were found to be relatively sensitive to the particular fit.

Having gained some experience in the application of the simplified second Born approximation the extension to molecular hydrogen was attempted. It was immediately apparent that the numerical methods used in the calculation of atomic scattering, were not useful for electron-molecule scattering. Problems occur in the evaluation of the final integral over $\mathbf{k}$ in the second Born terms. One way to avoid this problem is to numerically evaluate this integral. Programs were developed to numerically estimate the three dimensional integral. These were tested by calculating electron-helium amplitudes which were compared with the analytic results of chapter 6. Applying these methods to electron-H_2 scattering, it was found that although it is quite feasible to evaluate the required integrals numerically, it is not practical even for the simple

system of electron plus molecular hydrogen because of the extensive amount of computation required to achieve converged results.

An alternative discussed in chapter 8, which may be useful for simple molecular targets is to use a single center expansion of the interaction potential. This reduces the problem of scattering from a non-spherically symmetric molecular target, to the scattering of an electron from a pseudo-atom and thus allows the scattering amplitudes to be calculated more efficiently.

Target rotation and vibration must also be considered when dealing with molecular scattering. For scattering amplitudes calculated using the adiabatic nuclei approximation to be compared with experiment, some form of orientational averaging must be completed. A way to avoid this is to calculate partial wave scattering amplitudes so the final orientational integral reduces to a summation over partial waves.

Scattering amplitudes were also calculated using the Schwinger variational principle, for static exchange scattering of electrons from the ground state of helium. A method of calculating scattering amplitudes beyond the static exchange approximation within the Schwinger framework is proposed in chapter 8. This method uses the closure approximation to estimate the second Born like matrix elements required. It is argued that these ideas may be useful at intermediate energies, either as a stand alone method of calculation or as a method used in conjunction with a pseudostate expansion, to optimize the pseudostate basis.

Appendix A

Transformation to the Center of Mass Coordinate

Considering the classical two dimensional system depicted in fig A-1 which consists of two mass points moving relative the fixed coordinate system with origin O. The two mass points are assumed to interact via a conservative potential which depends only on their separation $\mathbf{r} = \mathbf{r_2} - \mathbf{r_1}$ and perhaps the derivative of $\mathbf{r}$ with respect to time, and higher derivatives.

The center of mass of the two particle system is

$$\mathbf{R} = \frac{1}{m_1 + m_2}\left(m_1\mathbf{r_1} + m_2\mathbf{r_2}\right). \tag{A.1}$$

The kinetic energy in the fixed coordinate frame O is

$$\begin{aligned} T &= \frac{1}{2}m_1\dot{\mathbf{r}}_1^2 + \frac{1}{2}m_2\dot{\mathbf{r}}_2^2 \\ &= \frac{1}{2}(m_1 + m_2)\dot{\mathbf{R}}^2 - T' \end{aligned} \tag{A.2}$$

where

$$T' = \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}(\dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1)^2. \tag{A.3}$$

The classical Hamiltonian for the system is now [121]

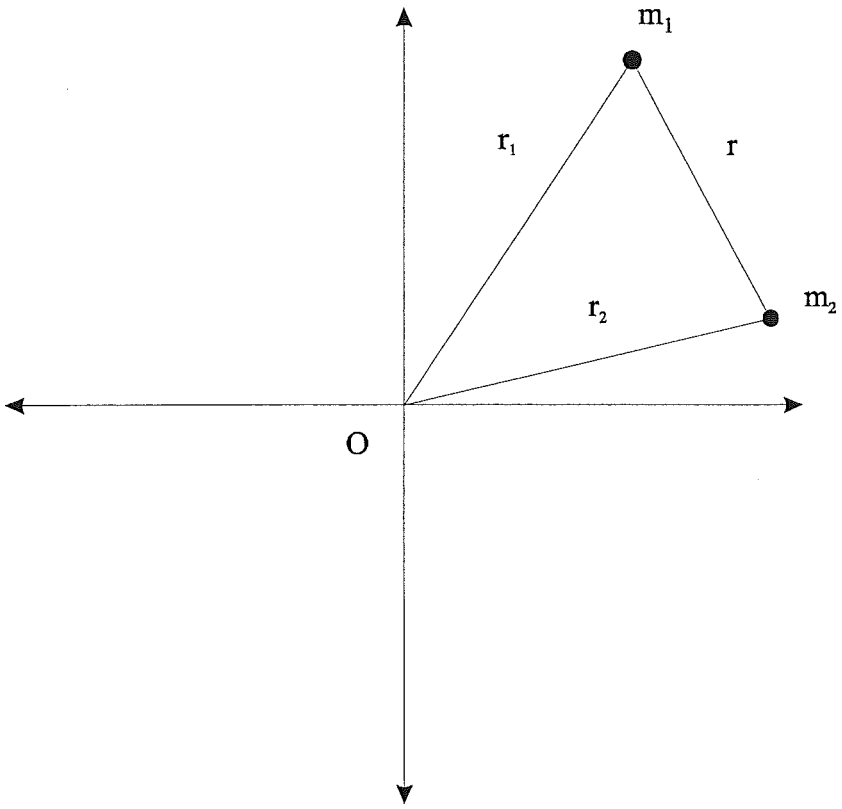


Figure A-1: Mechanical system of two classical particles

$$
\begin{aligned}
H &= T+V \\
&= \frac{1}{2}(m_1+m_2)\dot{\mathbf{R}}^2+\frac{1}{2}\frac{m_1m_2}{m_1+m_2}\dot{\mathbf{r}}^2+V(\mathbf{r},\dot{\mathbf{r}},\ldots) \\
&= H(\dot{\mathbf{R}})+H(\mathbf{r},\dot{\mathbf{r}},\ldots)
\end{aligned} \tag{A.4}
$$

Thus a separation of variables can be made and the equation of motion for the center of mass can be solved for using the total mass of the system m_1+m_2. The equation of motion of the relative coordinate $\mathbf{r}$ is solved for using the reduced mass,

$$
\mu = \frac{m_1m_2}{m_1+m_2} \tag{A.5}
$$

and does not involve the center of mass coordinate at all. Thus the two body problem has been reduced to two one body problems with the center of mass motion being particularly simple. The center of mass motion can always be subtracted out of any interacting system in free space, independent of the number of individual particles.

The same analysis can be carried out on the analogous quantum system using the conjugate momenta in the expressions for kinetic energy. That is eqn A.2 is now

$$
\begin{aligned}
T &= \frac{\mathbf{p_1}^2}{2m_1}+\frac{\mathbf{p_2}^2}{2m_2} \\
&= \ldots
\end{aligned} \tag{A.6}
$$

$\mathbf{p_1} = i\hbar\partial/\partial\mathbf{r_1}$ etc.

Extension systems containing to more than two particles follows accordingly [8].

Appendix B

The Green's Function

This appendix gives a brief introduction to Green's functions. An excellent text on this topic is *Green's Functions in Quantum Physics* by Economou [122].

B.1 The Time Independent Green's Function

The time independent Green's function $G(z)$, associated with the linear, Hermitian, time independent operator $\hat{L}$ is defined as the solution of the equation,

$$(z - \hat{L})G(z) = 1, \tag{B.1}$$

z is a complex variable. The spatial representation of this is

$$(z - L(\mathbf{r}))G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}') \tag{B.2}$$

$$G(\mathbf{r}, \mathbf{r}'; z) = \langle \mathbf{r}|\mathbf{G}(z)|\mathbf{r}'\rangle \tag{B.3}$$

$$L(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')\langle \mathbf{r}|\mathbf{L}|\mathbf{r}'\rangle. \tag{B.4}$$

Inverting eqn B.1 gives

$$G(z) = \frac{1}{(z - \hat{L})}. \tag{B.5}$$

The eigenfunctions of $|\hat{L}\rangle$, $|\phi_n\rangle$,

$$\hat{L}|\phi_n\rangle = \lambda_n|\phi_n\rangle, \tag{B.6}$$

form a complete set,

$$\sum_n |\phi_n\rangle\langle\phi_n| = 1 \tag{B.7}$$

so multiplying eqn B.5 by eqn B.7 gives

$$G(z) = [z - \hat{L}]^{-1} \sum_n |\phi_n\rangle\langle\phi_n|. \tag{B.8}$$

For a general function F the relation $F(\hat{L})|\phi_n\rangle = F(\lambda_n)|\phi_n\rangle$ so

$$G(z) = \sum_n \frac{|\phi_n\rangle\langle\phi_n|}{z - \lambda_n}. \tag{B.9}$$

If $\hat{L}$ contains both a discrete and continuous spectrum, eqn B.9 is written

$$G(z) = \sum_n \frac{|\phi_n\rangle\langle\phi_n|}{z - \lambda_n} + \int dn \frac{|\phi_n\rangle\langle\phi_n|}{z - \lambda_n}. \tag{B.10}$$

In this form it is obvious that G is an analytic function of the variable z except at the eigenvalues of $\hat{L}$. Because $\hat{L}$ is a Hermitian operator these eigenvalues, λ_n lie on the real axis. For the discrete spectrum of $\hat{L}$, $G(\lambda_n)$ exhibits simple poles and for the continuous spectrum, $G(\lambda_n)$ has a branch cut.

Although $G(z)$ is not defined on the real axis within the branch cut of the continuous spectrum of $\hat{L}$, two Green's functions $G^{\pm}(z)$ can be defined by the limiting procedure,

$$G^{+}(\lambda) = \lim_{\eta \to 0^{+}} G(\lambda + i\eta) \tag{B.11}$$

$$G^{-}(\lambda) = \lim_{\eta \to 0^{+}} G(\lambda - i\eta). \tag{B.12}$$

Given the solution to the homogeneous equation, eqn B.1, the solutions $G(z)$ can be used to solve the general inhomogeneous equation

$$(z - \hat{L})|u\rangle = |f\rangle \tag{B.13}$$

for a given function $|f\rangle$, where the solutions $|u\rangle$ satisfy the same boundary conditions as $G(z)$.

Now for $z = \lambda$ not in the spectrum of $\hat{L}$, $|u\rangle$ is given by

$$|u\rangle = |\phi_\lambda\rangle + G(\lambda)|f\rangle \tag{B.14}$$

which can be seen by substituting eqn B.14 into eqn B.13 and using eqn B.1,

$$\begin{aligned}
(\lambda - \hat{L})|u\rangle &= (\lambda - \hat{L})\left(|\phi_\lambda\rangle + G(\lambda)|f\rangle\right) \\
&= (\lambda - \hat{L})|\phi_\lambda\rangle + (\lambda - \hat{L})G(\mathbf{r}, \mathbf{r}'; \lambda)|f\rangle \\
&= 0 + 1|f\rangle
\end{aligned} \tag{B.15}$$

For $z = \lambda$ in the continuous spectrum of $\hat{L}$, the solution can be found in terms of the Green's functions $G^{\pm}(\lambda)$,

$$|u^{\pm}\rangle = |\phi\rangle + G^{\pm}(\lambda)|f\rangle. \tag{B.16}$$

The most important result for scattering theory is the Green's function for free motion. This is in the spatial representation, the solution of eqn B.2 with

$$L(\mathbf{r}) = -\frac{1}{2}\nabla^2. \tag{B.17}$$

So eqn B.2 is

$$[z + \frac{1}{2}\nabla^2]G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}'). \tag{B.18}$$

The solution is obtained by using eqn B.9. The complete set, $\{\phi_n\}$ of eigenfunctions of $L(\mathbf{r})$ are of the form

$$\langle \mathbf{r}|\mathbf{k}\rangle = \frac{1}{2\pi^{3/2}} \exp(i\mathbf{k}\cdot\mathbf{r}), \tag{B.19}$$

and

$$-\frac{1}{2}\nabla^2\phi = k^2\phi. \tag{B.20}$$

Equation B.9 now reads

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; z) &= \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\exp(i\mathbf{k}\cdot\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r}')}{z - k^2} \\ &= \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\exp(i\mathbf{k}\cdot\bar{\rho})}{z - k^2}, \end{aligned} \tag{B.21}$$

where

$$\bar{\rho} = \mathbf{r} - \mathbf{r}'. \tag{B.22}$$

Now taking the z axis along the vector $\bar{\rho}$,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; z) &= \frac{1}{(2\pi)^3} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} dk \frac{k^2 \exp(i\mathbf{k}\cdot\bar{\rho})}{z - k^2} \\ &= \frac{1}{4\pi^2} \int_0^{\infty} \frac{k^2 dk}{z - k^2} \int_0^{\pi} d\theta \sin\theta \exp(ik\rho\cos\theta) \\ &= \frac{1}{4\pi^2} \int_0^{\infty} \frac{k^2 dk}{z - k^2} \left(\frac{\exp(ik\rho) - \exp(-ik\rho)}{ik\rho}\right) \\ &= \frac{-1}{4\pi^2 i\rho} \int_0^{\infty} \frac{k\, dk}{k^2 - z} (\exp(ik\rho) - \exp(-ik\rho)) \\ &= \frac{-1}{4\pi^2 i\rho} \int_0^{\infty} \frac{k\, dk}{k^2 - z} 2\mathrm{Im}(\exp(ik\rho)) \end{aligned} \tag{B.23}$$

Now obviously the factor $k/(k^2 - z)$ is an odd function of k, so because $\mathrm{Im}(\exp(ik\rho))$ is also an odd function of k the limits if the integration can be extended to the infinite range, $-\infty \rightarrow \infty$.

$$\begin{aligned} I &= \int_0^\infty \frac{k\,dk}{k^2 - z} 2\mathrm{Im}(\exp(ik\rho)) \\ &= \frac{1}{2}\int_{-\infty}^\infty \frac{k\,dk}{k^2 - z} 2\mathrm{Im}(\exp(ik\rho)) \\ &= \int_{-\infty}^\infty \frac{k\,dk}{k^2 - z} \exp(ik\rho). \end{aligned} \tag{B.24}$$

The final expression is obtained by noting that the real part of $\exp(ik\rho)$ is an even function of k and so does not contribute to the integral.

Closing the integration path in the upper plane by a semicircle encloses one of the poles of the integrand $k = \pm\sqrt{z}$. Using the Cauchy residue theorem the integral can be completed. Denoting the root with positive imaginary part as $k = \sqrt{z}$,

$$\begin{aligned} I &= 2i\pi \frac{k\exp(ik\rho)}{k^2 - z}(k - \sqrt{z})\Big|_{k=\sqrt{z}} \\ &= i\pi \exp(i\sqrt{z}\rho). \end{aligned} \tag{B.25}$$

Finally, from eqn B.23

$$G(\mathbf{r}, \mathbf{r}'; z) = -\frac{1}{4\pi}\frac{\exp(i\sqrt{z}|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \tag{B.26}$$

If $z > 0$, eqn B.24 is not well defined, but the limits $G^{\pm}(\mathbf{r}, \mathbf{r}'; z)$ from eqns B.11 and B.12 are, so

$$G^{\pm}(\mathbf{r}, \mathbf{r}'; z) = -\frac{1}{4\pi}\frac{\exp(\pm i\sqrt{z}|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \tag{B.27}$$

B.2 Time Dependent Green's Functions

The first order, time dependent Green's function $g(t,t')$ associated with the linear, Hermitian, time independent operator $\hat{L}$, is defined as the solution of the equation,

$$\left(\frac{i}{c}\frac{\partial}{\partial t} - \hat{L}\right) g(t,t') = \delta(t-t'). \tag{B.28}$$

Now taking the Fourier transform of the function $g(t,t')$,

$$g(t,t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega(t-t')} g(\omega), \tag{B.29}$$

and substituting back into eqn B.28 gives

$$\begin{aligned}\left(\frac{i}{c}\frac{\partial}{\partial t} - \hat{L}\right) g(t,t') = \delta(t-t') &= \left(\frac{i}{c}\frac{\partial}{\partial t} - \hat{L}\right)\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega(t-t')} g(\omega) \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega(t-t')}\left(\frac{\omega}{c} - \hat{L}\right) g(\omega)\end{aligned} \tag{B.30}$$

Noting the definition of the Dirac delta function

$$\delta(t-t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{i\omega(t-t')}, \tag{B.31}$$

then

$$\left(\frac{\omega}{c} - \hat{L}\right) g(\omega) = 1. \tag{B.32}$$

From eqn B.1 it can be seen that

$$g(\omega) = G(\omega/c). \tag{B.33}$$

The functions $g^{\pm}(t,t')$ can be defined from the corresponding functions $G^{\pm}(z)$ as

$$g^{\pm}(t,t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega(t-t')} G^{\pm}(\omega/c). \tag{B.34}$$

From the solution of the homogeneous partial differential equation,

$$\left(\frac{i}{c}\frac{\partial}{\partial t} - \hat{L}\right)|\phi(t)\rangle = 0, \tag{B.35}$$

where the solutions obey the same boundary conditions as $g(t,t')$, the corresponding inhomogeneous equation

$$\left(\frac{i}{c}\frac{\partial}{\partial t} - \hat{L}\right)|\psi(t)\rangle = |f(t)\rangle, \tag{B.36}$$

can be solved. Using $g^{\pm}(t,t')$,

$$|\psi^{(\pm)}(t)\rangle = |\phi(t)\rangle + \int dt' g^{\pm}(t,t')|f(t')\rangle. \tag{B.37}$$

This can be shown by substituting eqn B.37 into eqn B.36 and using eqns B.35 and B.28.

Finally it can be shown that the functions $g^{\pm}(t,t')$ are related to the time evolution operator $U(t-t')$ where

$$U(t-t') = \exp(-ic\hat{L}(t-t')). \tag{B.38}$$

so that for a function $|\phi(t)\rangle$ which is a solution of eqn B.35 at time t, the function

$$|\phi(t')\rangle = \int dt \left(\frac{i}{c}\right) g^{+}(t,t')|\phi(t)\rangle \tag{B.39}$$

is a solution of the same equation at the time $t' > t$. Similarly

$$|\phi(t')\rangle = \int dt \left(\frac{i}{c}\right) g^{-}(t,t')|\phi(t)\rangle \tag{B.40}$$

is a solution of eqn B.35 at the time $t' < t$.

B.3 Green's Functions and Perturbation Theory

For a Hamiltonian that can be written in the form

$$H = H_0 + H_1, \tag{B.41}$$

two Greens functions can be defined

$$G_0(z) = (z - H_0)^{-1} \tag{B.42}$$

$$\begin{aligned} G(z) &= (z - H)^{-1} \\ &= (z - H_0 - H_1)^{-1} \\ &= \left[(z - H_0)(1 - (z - H_0)^{-1} H_1)\right]^{-1} \\ &= [1 - G_0(z) H_1]^{-1} G_0(z). \end{aligned} \tag{B.43}$$

The term $[1 - G_0(z)H_1]^{-1}$ can be expanded giving

$$\begin{aligned} G(z) &= G_0 + G_0 H_1 G_0 + G_0 H_1 G_0 H_1 G_0 + \ldots \\ &= G_0 + G_0 H_1 (G_0 + G_0 H_1 G_0 + \ldots) \\ &= G_0 + G_0 H_1 G(z) \\ &= G_0 + (G_0 + G_0 H_1 G_0 + \ldots) H_1 G_0 \\ &= G_0 + G(z) H_1 G_0. \end{aligned} \tag{B.44}$$

Defining the operator $T(z)$ as

$$T(z) = H_1 G(z)(z - H_0) \tag{B.45}$$

then using eqn B.44 gives the expansion

$$T(z) = H_1 + H_1 G_0 H_1 + H_1 G_0 H_1 G_0 H_1 + \ldots \tag{B.46}$$

Further

$$T(z) = H_1 + H_1 G_0 H_1 + H_1 G_0 H_1 G_0 H_1 + \ldots$$

$$
\begin{aligned}
&= H_1 + H_1 G_0 (H_1 + H_1 G_0 H_1 + \ldots) \\
&= H_1 + H_1 G_0 T(z) \qquad \text{(B.47)} \\
&= H_1 + H_1 (G_0 + G_0 H_1 G_0 + \ldots) H_1 \\
&= H_1 + H_1 G(z) H_1 \qquad \text{(B.48)} \\
&= H_1 + (H_1 + H_1 G_0 H_1 + \ldots) G_0 H_1 \\
&= H_1 + T(z) G_0 H_1. \qquad \text{(B.49)}
\end{aligned}
$$

These equations are valid when z is not part of the spectrum of H_0. When z lies in the continuous spectrum of H_0, two operators $T^{\pm}$ can be defined

$$
T^{\pm}(z) = H_1 + H_1 G_0^{\pm} H_1 + H_1 G_0^{\pm} H_1 G_0^{\pm} H_1 + \ldots \qquad \text{(B.50)}
$$

and

$$
\begin{aligned}
T^{\pm}(z) &= H_1 + H_1 G_0^{\pm} T^{\pm}(z) \\
&= H_1 + H_1 G^{\pm}(z) H_1 \\
&= H_1 + T^{\pm}(z) G_0 H_1. \qquad \text{(B.51)}
\end{aligned}
$$

Now from eqn B.44,

$$
\begin{aligned}
H_1 G^{\pm} &= H_1 G_0^{\pm} + H_1 G_0^{\pm} H_1 G_0^{\pm} + H_1 G_0^{\pm} H_1 G_0^{\pm} H_1 G_0^{\pm} + \ldots \\
&= (H_1 + H_1 G_0^{\pm} H_1 + \ldots) G_0^{\pm} \\
&= T^{\pm} G_0^{\pm}, \qquad \text{(B.52)}
\end{aligned}
$$

and similarly

$$
G^{\pm} H_1 = G_0^{\pm} T^{\pm}. \qquad \text{(B.53)}
$$

B.4 Green's Functions and Scattering Theory

For a particle scattering off a fixed target, interacting via an interaction potential V, the Hamiltonian can be written

$$\hat{H} = \hat{H}_0 + V. \tag{B.54}$$

The time independent Schrödinger equation is given by

$$\begin{aligned} (E - \hat{H})|\psi\rangle &= 0 \\ (E - \hat{H}_0)|\psi\rangle &= V|\psi\rangle \end{aligned} \tag{B.55}$$

using eqn B.54. Equation B.55 is now in the form of eqn B.13 with

$$\begin{aligned} z &= E \\ \hat{L} &= \hat{H}_0 \\ |u\rangle &= |\psi\rangle \\ |f\rangle &= V|\psi\rangle \end{aligned}$$

so from eqn B.16, the solutions $|\psi^{\pm}\rangle$ ($\pm$ to distinguish the solutions associated with $G_0^{\pm}$) can immediately be written as

$$|\psi^{\pm}\rangle = |\phi\rangle + G_0^{\pm}(E)V|\psi^{\pm}\rangle. \tag{B.56}$$

The functions $|\phi\rangle$ are solutions of the equation

$$\hat{H}_0|\phi\rangle = E|\phi\rangle. \tag{B.57}$$

Equation B.56 is called the Lippman-Schwinger equation and can be solved giving

$$
\begin{aligned}
|\psi^{\pm}\rangle &= (1 - G_0^{\pm} V)^{-1} |\phi\rangle \\
&= |\phi\rangle + G_0^{\pm} V |\phi\rangle + G_0^{\pm} V G_0^{\pm} V |\phi\rangle + \ldots \\
&= |\phi\rangle + G_0^{\pm} (V|\phi\rangle + G_0^{\pm} V |\phi\rangle + \ldots) \\
&= |\phi\rangle + G_0^{\pm} T^{\pm} |\phi\rangle. \qquad \text{(B.58)}
\end{aligned}
$$

Comparing eqn B.56 and eqn B.58 it can be seen that

$$
T^{\pm} |\phi\rangle = V |\psi^{\pm}\rangle. \qquad \text{(B.59)}
$$

Appendix C

Free-Free Direct Integrals

The free-free direct integrals are of the form

$$I_d = \int\int d\mathbf{r}_0 d\mathbf{r}_1 e^{-i\mathbf{k}_2\cdot\mathbf{r}_0} e^{i\mathbf{k}_1\cdot\mathbf{r}_0} \frac{1}{r_{01}} f_{nlm}(\mathbf{r}_1) f_{n'l'm'}(\mathbf{r}_1), \tag{C.1}$$

the functions $f(\mathbf{r}_1)$ being either Slater or Cartesian Gaussian functions.

Eqn C.1 can immediately be reduced to an integral over $\mathbf{r}_1$ by applying Bethe's integral

$$\int d\mathbf{r}_0 \frac{e^{i\mathbf{K}\cdot\mathbf{r}_0}}{|\mathbf{r}_0 - \mathbf{r}_1|} = 4\pi \frac{e^{i\mathbf{K}\cdot\mathbf{r}_1}}{K^2} \tag{C.2}$$

so

$$I_d = \frac{4\pi}{K^2} \int d\mathbf{r}_1 e^{i\mathbf{K}\cdot\mathbf{r}_1} f_{nlm}(\mathbf{r}_1) f_{l'm'n'}(\mathbf{r}_1). \tag{C.3}$$

C.1 Slater Direct Integrals

Firstly considering two s-Slater functions eqn C.3 is

$$\begin{aligned} I_d &= \frac{4\pi}{K^2} \int d\mathbf{r}_1 e^{i\mathbf{K}\cdot\mathbf{r}_1} e^{-\alpha r_1} \\ &= \frac{4\pi}{K^2} \frac{2\alpha}{(K^2+\alpha^2)^2}. \end{aligned} \tag{C.4}$$

Now extension to higher order Slater functions can made by first noting the integral involving powers of r_1 can be obtained from the differential of the s-function result with respect to α.

$$\begin{aligned} I_d &= \frac{4\pi}{K^2}\int d\mathbf{r_1} e^{i\mathbf{K}\cdot\mathbf{r_1}} r_1^n e^{-\alpha r_1} \\ &= \frac{4\pi}{K^2}(-1)^n \frac{\partial^n}{\partial\alpha^n}\left(\int d\mathbf{r_1} e^{i\mathbf{K}\cdot\mathbf{r_1}} e^{-\alpha r_1}\right) \\ &= \frac{4\pi}{K^2}(-1)^n \frac{\partial^n}{\partial\alpha^n}\left(\frac{2\alpha}{(K^2+\alpha^2)^2}\right). \end{aligned} \tag{C.5}$$

Finally for $l, m \neq 0$, eqn C.3 is

$$I_d = \frac{4\pi}{K^2}\int d\mathbf{r_1} e^{i\mathbf{K}\cdot\mathbf{r_1}} f_n(r_1) Y_{lm}(\hat{\mathbf{r}_1}) f_{n'}(r_1) Y_{l'm'}(\mathbf{r_1}). \tag{C.6}$$

Expanding the plane wave as

$$e^{i\mathbf{K}\cdot\mathbf{r_1}} = 4\pi \sum_{LM} i^L j_L(Kr_1) Y^*_{LM}(\hat{\mathbf{r}_1}) Y_{LM}(\hat{\mathbf{K}}) \tag{C.7}$$

where $j_L(z)$ is a spherical harmonic, eqn C.6 is now

$$\begin{aligned} I_d &= \frac{4\pi}{K^2}\sum_{LM} i^L \int_0^\infty dr_1 r_1^2 j_L(Kr_1) f_n(r_1) f_{n'}(r_1) \\ &\quad \int d\hat{\mathbf{r}_1} Y_{lm}(\hat{\mathbf{r}_1}) Y_{l'm'}(\hat{\mathbf{r}_1}) Y^*_{LM}(\hat{\mathbf{r}_1}) Y_{LM}(\hat{\mathbf{K}}) \\ &= \frac{4\pi}{K^2}\sum_{LM} i^L \int_0^\infty dr_1 r_1^2 j_L(Kr_1) f_n(r_1) f_{n'}(r_1) \\ &\quad C(l,l',L,M;m,m') Y_{LM}(\hat{\mathbf{K}}) \end{aligned} \tag{C.8}$$

where $C(l,l',L,M;m,m')$ is the Clebsch-Gordan coefficient [123].

C.2 Gaussian Direct Integrals

Following section C.1, the initial case of two s-Gaussian functions centered at the origin is

$$
\begin{aligned}
I_d &= \frac{4\pi}{K^2}\int d\mathbf{r_1} e^{i\mathbf{K}\cdot\mathbf{r_1}} e^{-\alpha r_1^2} \\
&= \frac{4\pi}{K^2}\left(\frac{\pi}{\alpha}\right)^{3/2} e^{-K^2/4\alpha}.
\end{aligned} \tag{C.9}
$$

Higher order Cartesian Gaussian functions can be evaluated from the differential of eqn C.9 with respect to the components of the $\mathbf{K}$ vector

$$
\begin{aligned}
I_d &= \frac{4\pi}{K^2}\int d\mathbf{r_1} e^{i\mathbf{K}\cdot\mathbf{r_1}} x^l y^m z^n e^{-\alpha r_1^2} \\
&= \frac{4\pi}{K^2}\frac{\partial^l}{i^l \partial K_x^l}\frac{\partial^m}{i^m \partial K_y^m}\frac{\partial^n}{i^n \partial K_z^n}\left(\int d\mathbf{r_1} e^{i\mathbf{K}\cdot\mathbf{r_1}} e^{-\alpha r_1^2}\right) \\
&= \frac{4\pi}{K^2}\left(\frac{\pi}{\alpha}\right)^{3/2}\left(\frac{i}{2\sqrt{\alpha}}\right)^{l+m+n} e^{-K^2/4\alpha} \\
&\quad H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right) H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right)
\end{aligned} \tag{C.10}
$$

where $H_i(z)$ is the ith order Hermite polynomial.

Appendix D

Free-Free Exchange Integrals

D.1 Slater Exchange integrals

The integral required for the calculation of the first Born exchange scattering amplitudes (see section 6.1.1), for a basis of simple s-Slater functions, is

$$I_s = \int\int d\mathbf{r_0} d\mathbf{r_1} e^{-i\mathbf{k_2}\cdot\mathbf{r_0}} e^{-\beta r_0} \frac{1}{r_{01}} e^{-\alpha r_1} e^{i\mathbf{k_1}\cdot\mathbf{r_1}} \tag{D.1}$$

I_s is evaluated by firstly substituting for the $1/r_{01}$ term,

$$\frac{1}{r_{01}} = \frac{4\pi}{(2\pi)^3} \int \frac{d\mathbf{k}}{k^2} e^{-i\mathbf{k}\cdot(\mathbf{r_0}-\mathbf{r_1})}. \tag{D.2}$$

The integrals over $\mathbf{r_0}$ and $\mathbf{r_1}$ are now separable and can be completed (see appendix C), giving

$$I_s = \frac{(4\pi)^3}{(2\pi)^3} \int \frac{d\mathbf{k}}{k^2} \frac{2\beta}{((\mathbf{k}+\mathbf{k_2})^2+\beta^2)^2} \frac{2\alpha}{((\mathbf{k}-\mathbf{k_1})^2+\alpha^2)^2} \tag{D.3}$$

Noting the integral

$$I(\lambda;\mathbf{k_1},\mu_1;\mathbf{k_2},\mu_2) = \int d\mathbf{k}[(|\mathbf{k}-\mathbf{k_1}|^2+\mu_1^2)(|\mathbf{k}-\mathbf{k_2}|^2+\mu^2)(k^2+\lambda^2)]^{-1}, \tag{D.4}$$

which has been evaluated analytically by Lewis (see appendix E), then

$$I_s = \frac{(4\pi)^3}{(2\pi)^3}\frac{\partial^2}{\partial\alpha\partial\beta}\left[I(0;\mathbf{k_1},\alpha;-\mathbf{k_2},\beta)\right] \tag{D.5}$$

The second differential of the integral $I(\mathbf{k};\mathbf{k_1},\mu_1;\mathbf{k_2},\mu_2)$ has also been calculated, see appendix F.

D.2 Gaussian Exchange integrals

The corresponding Gaussian exchange integral, for s-Gaussian functions centered at the origin, is

$$I_g = \int\int d\mathbf{r_0}d\mathbf{r_1}e^{-i\mathbf{k_2}\cdot\mathbf{r_0}}e^{-\beta r_0^2}\frac{1}{r_{01}}e^{-\alpha r_1^2}e^{i\mathbf{k_1}\cdot\mathbf{r_1}} \tag{D.6}$$

Evaluation of I_g proceeds in exactly the same manner as I_s above. The substitution of eqn D.2 is made and the integrals over $\mathbf{r_0}$ and $\mathbf{r_1}$ are completed leaving

$$\begin{aligned} I_g &= \frac{4\pi}{(2\pi)^3}\left(\frac{\pi}{\beta}\right)^{3/2}\left(\frac{\pi}{\alpha}\right)^{3/2}\int\frac{d\mathbf{k}}{k^2}e^{-(\mathbf{k}+\mathbf{k_2})^2/4\beta}e^{-(\mathbf{k}+\mathbf{k_1})^2/4\alpha} \\ &= \frac{4\pi}{(2\pi)^3}\left(\frac{\pi}{\beta}\right)^{3/2}\left(\frac{\pi}{\alpha}\right)^{3/2}e^{-k_2^2/4\beta}e^{-k_1^2/4\alpha}\int\frac{d\mathbf{k}}{k^2}e^{-ak^2}e^{-2\mathbf{k}\cdot\mathbf{C}} \end{aligned} \tag{D.7}$$

where

$$a = \frac{\alpha+\beta}{4\alpha\beta} \quad \text{and} \quad \mathbf{C} = \frac{\mathbf{k_2}}{4\beta}+\frac{\mathbf{k_1}}{4\alpha} \tag{D.8}$$

Transforming to spherical polar coordinates with the z axis along the $\mathbf{C}$ vector gives

$$\begin{aligned} I_g &= \frac{4\pi}{(2\pi)^3}\left(\frac{\pi}{\beta}\right)^{3/4}\left(\frac{\pi}{\alpha}\right)^{3/2}e^{-k_2^2/4\beta}e^{-k_1^2/4\alpha}\int_0^\infty dke^{-ak^2}\int_0^\pi \sin\theta e^{-2kC\cos\theta}\int_0^{2\pi}d\phi \\ &= \frac{8\pi^2}{(2\pi)^3}\left(\frac{\pi}{\beta}\right)^{3/4}\left(\frac{\pi}{\alpha}\right)^{3/2}e^{-k_2^2/4\beta}e^{-k_1^2/4\alpha}\int_0^\infty dke^{-ak^2}\frac{1}{kC}\mathrm{sh}(2Ck) \end{aligned}$$

$$= \frac{8\pi^2}{(2\pi)^3}\left(\frac{\pi}{\beta}\right)^{3/4}\left(\frac{\pi}{\alpha}\right)^{3/2} e^{-k_2^2/4\beta} e^{-k_1^2/4\alpha} \frac{\pi}{2iC}\mathrm{erf}\left(\frac{iC}{\sqrt{a}}\right), \tag{D.9}$$

the final integral over k being obtained from [124].

Appendix E

Analytic Second Born Integrals

Following the method of Lewis [91], the integral to be calculated is

$$I(\lambda;\mathbf{k_1},\mu_1;\mathbf{k_2},\mu_2) = \int d\mathbf{k}[(|\mathbf{k}-\mathbf{k_1}|^2+\mu_1^2)(|\mathbf{k}-\mathbf{k_2}|^2+\mu_2^2)(k^2+\lambda^2)]^{-1}. \tag{E.1}$$

Firstly using the Feynman relation

$$\frac{1}{ab} = \int_0^1 dz[az+b(1-z)]^{-2}, \tag{E.2}$$

and

$$\begin{aligned}
&(|\mathbf{k}-\mathbf{k_1}|^2+\mu_1^2)z + (|\mathbf{k}-\mathbf{k_2}|^2+\mu_2^2)(1-z) \\
&= k^2z - 2z\mathbf{k}\cdot\mathbf{k_1} + k_1^2z + \mu_1^2z + k^2(1-z) - 2(1-z)\mathbf{k}\cdot\mathbf{k_2} \\
&\quad + k_2^2(1-z) + \mu_2^2(1-z) \\
&= k^2 - 2\mathbf{k}\cdot(\mathbf{k_1}z+\mathbf{k_2}(1-z)) + (k_1^2z^2 + 2z(1-z)\mathbf{k_1}\cdot\mathbf{k_2} + k_2^2(1-z)^2) \\
&\quad + z(1-z)(k_1^2 - 2\mathbf{k_1}\cdot\mathbf{k_2} + k_2^2) + \mu_1^2z + \mu_2^2(1-z) \\
&= |\mathbf{k}-\mathbf{Q}|^2 + \Delta^2,
\end{aligned} \tag{E.3}$$

$$\mathbf{Q} = \mathbf{k_1} z + \mathbf{k_2}(1-z), \tag{E.4}$$

$$\Delta^2 = |\mathbf{k_1} - \mathbf{k_2}|^2 z(1-z) + \mu_1^2 z + \mu_2^2(1-z). \tag{E.5}$$

Now

$$\begin{aligned} I &= \int_0^1 dz \int d\mathbf{k}[(k^2+\lambda^2)(|\mathbf{k}-\mathbf{Q}|^2+\Delta^2)^2]^{-1} \\ &= -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\int d\mathbf{k}[(k^2+\lambda^2)(|\mathbf{k}-\mathbf{Q}|^2+\Delta^2)]^{-1}. \end{aligned} \tag{E.6}$$

Taking the z-axis of the $\mathbf{k}$ frame, to lie along the vector $\mathbf{Q}$, eqn E.6 becomes, with $u = \cos\theta$,

$$\begin{aligned} I &= -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\left(\int_{-1}^1 du \int_0^\infty k^2 dk \int_0^{2\pi} d\phi[(k^2+\lambda)]^{-1}\right. \\ &\quad \left.[(k^2 - 2kQu + Q^2 + \Delta^2)]^{-1}\right) \\ &= -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\left(2\pi\int_{-1}^1 du \int_0^\infty k^2 dk[(k^2+\lambda)]^{-1}\right. \\ &\quad \left.[(k^2 - 2kQu + Q^2 + \Delta^2)]^{-1}\right). \end{aligned} \tag{E.7}$$

Completion of the contour of k by a semi-circle in the upper half-plane, and evaluation the integrand at the two poles thus enclosed,

$$k = i\lambda, \qquad k = Qu + i(Q^2u^2 - Q^2 - \Delta^2)^{1/2}, \tag{E.8}$$

gives

$$I = -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\left(\int_{-1}^1 \pi^2 \frac{du}{\lambda + \Delta - iQu}\right). \tag{E.9}$$

The integral over u is easily completed to give

$$
\begin{aligned}
I &= -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\left(\frac{i\pi^2}{Q}\ln\left(\frac{\lambda+\Delta-iQ}{\lambda+\Delta+iQ}\right)\right) \\
&= -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\left(\frac{i\pi^2}{Q}\frac{2iQ}{\lambda^2+\Delta^2+2\lambda\Delta+Q^2}\right) \\
&= \pi^2\int_0^1 dz \frac{1}{\Delta}\left(\frac{1}{\lambda^2+(k_1^2+\mu_1^2)z+(k_2^2+\mu_2^2)(1-z)+2\lambda\Delta}\right). \qquad \text{(E.10)}
\end{aligned}
$$

The final integral over z can be completed by reducing the integrand to rational form, using a number of linear fractional transformations.

The final result is

$$
I(\lambda;\mathbf{k_1},\mu_1;\mathbf{k_2}\mu_2) = \pi^2(\beta^2-\alpha\gamma)^{-1/2}\ln\left(\frac{\beta+(\beta^2-\alpha\gamma)^{1/2}}{\beta-(\beta^2-\alpha\gamma)^{1/2}}\right). \qquad \text{(E.11)}
$$

$$
\begin{aligned}
\alpha\gamma &= [(\mathbf{k_1}-\mathbf{k_2})^2+(\mu_1+\mu_2)^2][k_1^2+(\mu_1+\lambda)^2] \\
&\quad [k_2^2+(\mu_2+\lambda)^2], \qquad \text{(E.12)}
\end{aligned}
$$

$$
\begin{aligned}
\beta &= \lambda[(\mathbf{k_1}-\mathbf{k_2})^2+(\mu_1+\mu_2)^2]+\mu_2(\lambda^2+k_1^2+\mu_1^2) \\
&\quad +\mu_1(\lambda^2+k_2^2+\mu_2^2) \qquad \text{(E.13)}
\end{aligned}
$$

Appendix F

Second Differential of the Integral $I(\lambda; \mathbf{k_1}, \mu_1; \mathbf{k_2}, \mu_2)$

The integral $I(\lambda; \mathbf{k}_1, \mu_1; \mathbf{k_2}, \mu_2)$ is defined in eqn E.1 with the solution given by eqn E.11. The integral

$$I_d(\lambda; \mathbf{k}_1, \mu_1; \mathbf{k_2}, \mu_2) = \int d\mathbf{k}[(|\mathbf{k} - \mathbf{k_1}|^2 + \mu_1^2)^2(|\mathbf{k} - \mathbf{k_2}|^2 + \mu^2)^2(k^2 + \lambda^2)]^{-1}. \tag{F.1}$$

is required for a number of applications. I_d is evaluated by noting

$$I_d(\lambda; \mathbf{k}_1, \mu_1; \mathbf{k_2}, \mu_2) = \frac{1}{2\mu_1}\frac{1}{2\mu_2}\frac{\partial^2}{\partial\mu_1\partial\mu_2} I(\lambda; \mathbf{k_1}, \mu_1; \mathbf{k_2}, \mu_2). \tag{F.2}$$

The second differential is evaluated by writing the expression for I in the form

$$\begin{aligned} I(\lambda; \mathbf{k}_1, \mu_1; \mathbf{k_2}\mu_2) &= \pi^2(\beta^2 - \alpha\gamma)^{-1/2} \ln\left(\frac{\beta + (\beta^2 - \alpha\gamma)^{1/2}}{\beta - (\beta^2 - \alpha\gamma)^{1/2}}\right) \\ &= \pi^2\phi_{00}\psi_{00} \end{aligned} \tag{F.3}$$

$$\phi_{00} = \frac{1}{\sqrt{A_{00}}} \qquad \psi_{00} = \frac{1}{i}\ln\left(\frac{1+i(Q_{00}-1)^{1/2}}{1-i(Q_{00}-1)^{1/2}}\right) \tag{F.4}$$

and

$$A_{00} = \alpha\gamma - \beta^2 \qquad Q_{00} = 1 + \frac{A_{00}}{B_{00}} \qquad B_{00} = \beta \tag{F.5}$$

Now

$$I_d(\lambda; \mathbf{k_1}, \mu_1; \mathbf{k_2}, \mu_2) = \pi^2(\phi_{00}\psi_{11} + \phi_{10}\psi_{01} + \phi_{01}\psi_{10} + \phi_{11}\psi_{00}). \tag{F.6}$$

$$\begin{aligned}
\phi_{00} &= \frac{1}{\sqrt{A_{00}}} \\
\phi_{10} &= -\frac{A_{10}}{2A_{00}^{3/2}} \\
\phi_{01} &= -\frac{A_{01}}{2A_{00}^{3/2}} \\
\phi_{11} &= \frac{\phi_{00}}{2A_{00}^2}\left(\frac{3}{2}A_{10}A_{01} - A_{11}A_{00}\right)
\end{aligned} \tag{F.7}$$

$$\begin{aligned}
\psi_{00} &= \frac{1}{i}\ln\left(\frac{1+i(Q_{00}-1)^{1/2}}{1-i(Q_{00}-1)^{1/2}}\right) \\
\psi_{10} &= \frac{Q_{10}}{Q_{00}(Q_{00}-1)^{1/2}} \\
\psi_{01} &= \frac{Q_{01}}{Q_{00}(Q_{00}-1)^{1/2}} \\
\psi_{11} &= \frac{1}{Q_{00}(Q_{00}-1)^{1/2}}\left(Q_{11} - Q_{10}Q_{01}\left(\frac{1}{Q_{00}} + \frac{1}{2(Q_{00}-1)}\right)\right)
\end{aligned} \tag{F.8}$$

$$\begin{aligned}
Q_{00} &= 1 + \frac{A_{00}}{B_{00}^2} \\
Q_{10} &= \frac{1}{B_{00}^3}\left(A_{10}B_{00} - 2A_{00}B_{10}\right) \\
Q_{01} &= \frac{1}{B_{00}^3}\left(A_{01}B_{00} - 2A_{00}B_{01}\right)
\end{aligned}$$

$$Q_{11} = \frac{1}{B_{00}^2}\left(A_{11} - \frac{2}{B_{00}}\left(A_{00}B_{11} + A_{10}B_{01} + A_{01}B_{10}\right) + \frac{6}{B_{00}^2}\left(A_{00}B_{10}B_{01}\right)\right)$$

A_{00} and B_{00} begin defined in eqn F.5.

The expressions for $\alpha\gamma$ and β are given in eqns E.12 and E.13 in terms of μ_1 and μ_2. Thus the differentials of A_{00} and B_{00} with respect to μ_1 and μ_2 and their the second differentials can be evaluated and substituted into the equations above.

Appendix G

Evaluation of the second Born Integrals for Gaussian charge distributions

The integral to be evaluated is,

$$I_g = \int d\mathbf{k} \frac{e^{-b_i|\mathbf{k_1}-\mathbf{k}|^2} e^{-b_j|\mathbf{k}-\mathbf{k_2}|^2}}{|\mathbf{k_1}-\mathbf{k}|^2|\mathbf{k}-\mathbf{k_2}|^2(k^2-\lambda^2)}. \tag{G.1}$$

Two possible routes to the evaluation of this integral are evident. The first, starts with the Feynman identity for the factor in the denominator,

$$\begin{aligned} \frac{1}{|\mathbf{k_1}-\mathbf{k}|^2|\mathbf{k}-\mathbf{k_2}|^2} &= \int_0^1 dz \left(\frac{1}{z|\mathbf{k_1}-\mathbf{k}|^2 + (1-z)|\mathbf{k}-\mathbf{k_2}|^2} \right)^2 \\ &= \int_0^1 dz \left(\frac{1}{|k-\mathbf{Q}|^2 + \Delta^2} \right)^2 \end{aligned} \tag{G.2}$$

where $\mathbf{Q} = z|\mathbf{k_1}-\mathbf{k}| + (1-z)|\mathbf{k_2}-\mathbf{k}|$ and $\Delta^2 = z(1-z)(\mathbf{k_1}-\mathbf{k_2})^2$. Eqn G.1 can now be written

$$
\begin{aligned}
I_g &= -\frac{1}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\int d\mathbf{k}\frac{e^{-b_i|\mathbf{k_1}-\mathbf{k}|^2}e^{-b_j|\mathbf{k}-\mathbf{k_2}|^2}}{(|\mathbf{k}-\mathbf{Q}|^2+\Delta^2)(k^2-\lambda^2)} \\
&= -\frac{e^{-C}}{2}\int_0^1 dz \frac{1}{\Delta}\frac{\partial}{\partial\Delta}\int d\mathbf{k}\frac{e^{-ak^2}e^{\mathbf{k}\cdot\mathbf{P}}}{(|\mathbf{k}-\mathbf{Q}|^2+\Delta^2)(k^2-\lambda^2)}.
\end{aligned} \tag{G.3}
$$

$$
C = b_i k_1^2 + b_j k_2^2 \qquad \mathbf{P} = -2(\mathbf{k_1}+\mathbf{k_2}) \qquad a = b_i + b_j \tag{G.4}
$$

This has the same form as eqn E.6 derived by Lewis [91], the difference being the $e^{-ak^2}e^{\mathbf{k}\cdot\mathbf{P}}$ factor in eqn G.3. To proceed, the integral over $\mathbf{k}$ is completed leaving the final integral over the Feynman parameter, z to be evaluated. Unfortunately, the integral over $\mathbf{k}$ can not be calculated in a simple closed form due to the presence of the $e^{\mathbf{k}\cdot\mathbf{P}}$ term, excluding this method as a possible route to the calculation of I_g.

Lewis [91] describes a method for calculating the second Born integrals

$$
I_g = \int \frac{e^{-\beta_i K_1^2}e^{-\beta_j K_2}d\mathbf{k}}{K_1^2 K_2^2(k^2+\lambda)} \tag{G.5}
$$

for $\beta_i = \beta_j$ The calculation for $\beta_i \neq \beta_j$, starts with the expression for the first Born amplitudes

$$
\begin{aligned}
f^{(0)}(K) &= \frac{e^{-\beta K^2}}{K^2} \\
&= \frac{F(K)}{K^2} \\
&= \frac{1}{K^2}\frac{1}{i\pi}\int_C ds \frac{sF(s)}{(K^2-s^2)}.
\end{aligned} \tag{G.6}
$$

The contour C is the real axis, with the poles at $s = \pm K$ being avoided by passing above. Now, combining the two terms from eqn G.5,

$$
F(K_1)F(K_2) = e^{-A}e^{-(\mathbf{k}-\mathbf{R})^2} \tag{G.7}
$$

where

$$A = \beta_i k_1^2 + \beta_j k_2^2 - \left(\frac{\beta_i \mathbf{k_1} + \beta_j \mathbf{k_2}}{\beta_i \beta_j}\right)^2 \qquad \mathbf{R}\frac{\beta_i \mathbf{k_1} + \beta_j \mathbf{k_2}}{\beta_i \beta_j}. \tag{G.8}$$

Using eqn G.6 in eqn G.5, thus leads to the expression

$$I_g = \lim_{\delta \to 0+} \frac{e^{-A}}{i\pi} \int_C ds\, s e^{-s^2} \int d\mathbf{k} \frac{1}{abcf} \tag{G.9}$$

$$a = K_1^2 + \delta^2 \qquad b = K_2^2 + \delta^2 \qquad c = k^2 + \lambda^2$$
$$f = |\mathbf{k} - \mathbf{R}|^2 - s^2. \tag{G.10}$$

Unfortunately, only for the case $\beta_i = \beta_j$ can eqn G.9 be reduces to three denominator integrals, which are required to proceed.

A final possibility for the evaluation of I_g is to leave the factors $F(K_1)F(K_2)$, uncombined in eqn G.5. Applying eqn G.6 twice gives

$$I_g = \lim_{\delta \to 0+} \frac{-1}{\pi^2} \int_C ds\, sF(s) \int_C dt\, tF(t) \int \frac{d\mathbf{k}}{abcde} \tag{G.11}$$

$$a = K_1^2 + \delta^2 \qquad b = K_2^2 + \delta^2 \qquad c = k^2 + \lambda^2$$
$$d = K_1^2 - s^2 \qquad e = K_2^2 - t^2. \tag{G.12}$$

Using partial fractions to reduce eqn G.11 gives,

$$\begin{aligned} I_g \;=\; & \lim_{\delta \to 0+} \frac{-1}{\pi^2} \int_C ds\, sF(s) \int_C dt\, tF(t) \left[\int \frac{d\mathbf{k}}{abc}\right. \\ & \left. - \int \frac{d\mathbf{k}}{bcd} - \int \frac{d\mathbf{k}}{ace} + \frac{d\mathbf{k}}{cde}\right] \end{aligned} \tag{G.13}$$

All the integrals over $\mathbf{k}$ are of the form

$$I = \int \frac{d\mathbf{k}}{(K_1^2 + c_1^2)(K_2^2 + c_2^2)(k^2 + \lambda^2)} \tag{G.14}$$

the solution of which has been given by Lewis. The final contour integrals, over s and t, are complicated integrals of the function $I(\lambda; \mathbf{k_1}, t; \mathbf{k_2}, t)$ multiplied by $\exp(-\beta_i s^2)$ and $\exp(-\beta_j t^2)$ factors. It is not envisaged that analytic evaluation of the final integrals is feasible but it may be possible to complete these integrals numerically.

Appendix H

The Levenberg-Marquardt Method

The problem to be solved is the fitting of a set of N data points (x_i, y_i), to a non-linear function of the independent variable, x. Denoting the nonlinear function as

$$y = y(c_1, c_2, \ldots, c_n; x) \tag{H.1}$$

where the coefficients $\{c_i\}$, are varied to give the best fit to the available data. The set of coefficients $\{c_i\}$ can be written as the vector $\mathbf{c}$.

The function of merit, χ^2 is defined as

$$\chi^2(\mathbf{c}) = \sum_{i=1}^{N} \left[\frac{y_i - y(\mathbf{c}; x_i)}{\sigma_i} \right]^2 . \tag{H.2}$$

The σ_i are the standard deviations for the individual datapoints (x_i, y_i). The problem now is to minimize the function $\chi^2(\mathbf{c})$ with respect to the set of coefficients $\mathbf{c}$.

The vector of gradients $\boldsymbol{\beta}$, with respect to the coefficients is

$$\begin{aligned} -2\beta_k &= \frac{\partial \chi^2}{\partial c_k} \\ &= -2 \sum_{i=1}^{N} \frac{[y_i - y(\mathbf{c}; x_i)]}{\sigma_i^2} \frac{\partial y(\mathbf{c}; x_i)}{\partial c_i} \qquad k = 1, 2, \ldots, n \end{aligned} \tag{H.3}$$

When the χ^2 function is minimized with respect to the c_i this vector, $\boldsymbol{\beta}$ is the null vector.

The matrix of second derivatives is

$$\begin{aligned} 2\Lambda_{kl} &= \frac{\partial^2 \chi^2}{\partial c_k \partial c_l} \\ &= 2\sum_{i=1}^{N} \frac{1}{\sigma_i^2} \left[[y_i - y(\mathbf{c}; x_i)] \frac{\partial^2 y(\mathbf{c}; x_i)}{\partial c_k \partial c_l} - \frac{\partial t(\mathbf{c}; x_i)}{\partial c_k} \frac{\partial y(\mathbf{c}; x_i)}{\partial c_l} \right]. \end{aligned} \tag{H.4}$$

The matrix $\mathbf{\Lambda}$ is just one-half the Hessian matrix of the function $y(\mathbf{c}; x)$.

H.1 Inverse Hessian Method

The Taylor expansion of an arbitrary function f, about the point $\mathbf{p}$, with coordinates $\mathbf{x}$ is,

$$f(\mathbf{x}) = f(\mathbf{p}) + \sum_i \frac{\partial f}{\partial x_i} x_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 f}{\partial x_i \partial x_j} x_i x_j + \ldots \tag{H.5}$$

Now for a point $\mathbf{q}$ sufficiently close to $\mathbf{p}$, the summation in eqn H.5 can be truncated to give

$$f(\mathbf{q}) \approx f(\mathbf{p}) + \sum_i \left(\left. \frac{\partial f}{\partial q_i} \right|_{q_i = p_i} \right) q_i + \frac{1}{2} \sum_{ij} \left(\left. \frac{\partial^2 f}{\partial q_i \partial q_j} \right|_{q_i = p_i, q_j = p_j} \right) q_i q_j, \tag{H.6}$$

or in vector notation

$$f(\mathbf{q}) \approx c - \mathbf{b} \cdot \mathbf{q} + \frac{1}{2} \mathbf{q} \cdot \mathbf{A} \cdot \mathbf{q}. \tag{H.7}$$

$$c = f(\mathbf{p}) \qquad \mathbf{b} = -\left. \nabla f \right|_{\mathbf{p}} \qquad \mathbf{A} = \left. \frac{\partial^2 f}{\partial x_i \partial x_j} \right|_{\mathbf{p}} \tag{H.8}$$

From eqn H.7

$$\begin{aligned} \left. \nabla f \right|_{\mathbf{q}} &= \nabla \left[c - \mathbf{b} \cdot \mathbf{q} + \frac{1}{2} \mathbf{q} \cdot \mathbf{A} \cdot \mathbf{q} \right] \\ &= -\mathbf{b} + \mathbf{A} \cdot \mathbf{q}. \end{aligned} \tag{H.9}$$

Now taking $f(\mathbf{x})$ to be the function $\chi^2(\mathbf{c})$ of eqn H.2 and $\mathbf{c_m}$ to be the vector which

minimizes $\chi^2(\mathbf{c})$, then for a vector bfc_p sufficiently close to $\mathbf{c_m}$,

$$\begin{aligned}\chi^2(\mathbf{c_m}) &\approx \chi^2(\mathbf{c_p}) + \sum_i \left(\left.\frac{\partial \chi^2}{\partial c_i}\right|_{\mathbf{c_p}} \right) c_{i(m)} + \frac{1}{2}\sum_{ij} \left(\left.\frac{\partial^2 \chi^2}{\partial c_i \partial c_j}\right|_{\mathbf{c_p}} \right) c_{i(m)} c_{j(m)} \\ &= \chi^2(\mathbf{c_p}) - 2\boldsymbol{\beta}\cdot\mathbf{c_m} + \mathbf{c_m}\cdot\boldsymbol{\Lambda}\cdot\mathbf{c_m} \end{aligned} \tag{H.10}$$

using eqns H.3 and H.4. $\boldsymbol{\beta}$ and $\boldsymbol{\Lambda}$ both being evaluated at the point $\mathbf{c_p}$. From eqn H.9

$$\nabla\chi^2(\mathbf{c_m}) = -2\boldsymbol{\beta} + \boldsymbol{\Lambda}\cdot\mathbf{c_m}, \tag{H.11}$$

but by definition the gradient of χ^2 at $\mathbf{c_m}$ vanishes, so

$$\boldsymbol{\Lambda}\cdot\mathbf{c_m} = 2\boldsymbol{\beta}. \tag{H.12}$$

Again using eqn H.9,

$$\nabla\chi^2(\mathbf{c_p}) = -2\boldsymbol{\beta} + \boldsymbol{\Lambda}\cdot\mathbf{c_p}. \tag{H.13}$$

or

$$\boldsymbol{\Lambda}\cdot\mathbf{c_p} = \nabla\chi^2(\mathbf{c_p}) + 2\boldsymbol{\beta}. \tag{H.14}$$

Subtracting eqn H.14 from eqn H.12 and multiplying on the left by $[\Lambda]^{-1}$ gives

$$\mathbf{c_m} - \mathbf{c_p} = [\boldsymbol{\Lambda}]^{-1}[-\nabla\chi^2(\mathbf{c_p})]. \tag{H.15}$$

Thus if $\mathbf{c_p}$ is sufficiently close to $\mathbf{c_m}$ for eqn H.10 to be reasonable, the vector $\mathbf{c_m}$ can be obtained from eqn H.15 by evaluation of the gradient vector $\nabla\chi^2(\mathbf{c_p})$ and the inverse of the Hessian matrix $[\boldsymbol{\Lambda}]^{-1}$, both evaluated at $\mathbf{c_p}$. This procedure can be continued by taking $\mathbf{c_m}$ as the $\mathbf{c_p}$ of the next iteration, and continuing until no further change occurs in the vector $\mathbf{c_m}$ or $\mathbf{c_p}$.

H.2 Method of Steepest Descent

Given a function $f(\mathbf{c})$ of the vector of coefficients $\mathbf{c}$, the vector with elements

$$\mathbf{b} = -\nabla f(\mathbf{c}) \tag{H.16}$$

evaluated at the point $\mathbf{c_p}$ gives local gradient at that point. Following this vector across the surface $f(\mathbf{c})$, initially, reduces the value of $f(\mathbf{c})$. At some point along this line the function obtains a minimum. If this point is taken as the new point $\mathbf{c_p}$, the vector $\mathbf{b}$ can again be evaluated and a line minimization along the new direction can be completed and the procedure iterated until the minimum of the function $f(\mathbf{c})$ is obtained.

Thus the iteration of the coefficients takes the form

$$\mathbf{c_{i+1}} = \mathbf{c_i} - \alpha_i \nabla f(\mathbf{c_i}). \tag{H.17}$$

The constant α_i being determined by the particular line minimization.

This 'Method of Steepest Descent' does not assume any form for the function $f(\mathbf{c})$ so can be useful when the starting point is far from the minimum.

H.3 The Levenberg-Marquardt Method

The Levenberg-Marquardt combines the inverse Hessian method and the method of steepest descent. The iteration formula for the inverse Hessian method is, see eqn H.15

$$\mathbf{c_{i+1}} = \mathbf{c_i} + \mathbf{\Lambda}^{-1} \cdot \boldsymbol{\beta}, \tag{H.18}$$

Defining the vector of increments $\delta\mathbf{c}$ as

$$\delta\mathbf{c} = \mathbf{c_{i+1}} - \mathbf{c_i} \tag{H.19}$$

then

$$\delta\mathbf{c} = \mathbf{\Lambda}^{-1} \cdot \boldsymbol{\beta}, \tag{H.20}$$

or

$$\mathbf{\Lambda} \cdot \delta \mathbf{c} = \boldsymbol{\beta}. \tag{H.21}$$

The steepest descent method can now be written as

$$\delta \mathbf{c} = \alpha \boldsymbol{\beta}. \tag{H.22}$$

The Levenberg-Marquardt method starts by noting that α can be set to any particular value less than the line minima of the particular iteration, and in fact can be used as a variable. Secondly, because $\chi^2(\mathbf{c})$ is dimensionless, the terms β_k have dimension $1/c_k$, see eqn H.3. Now the individual terms from eqn H.22 are

$$\delta c_k = \alpha b_k. \tag{H.23}$$

Introducing a factor γ_k which has the dimension c_k^2 gives

$$\delta c_k = \alpha \gamma_k b_k. \tag{H.24}$$

A suitable set of terms γ_k, with the correct dimension is given by the inverse diagonal elements of the matrix $\mathbf{\Lambda}$, $1/\Lambda_{kk}$, see eqn H.4. So

$$\delta c_k = \frac{1}{\epsilon \Lambda_{kk}} \beta_k \tag{H.25}$$

$(\alpha = 1/\epsilon)$ or

$$\epsilon \Lambda_{kk} \delta c_k = \beta_k. \tag{H.26}$$

Finally eqns H.21 and H.26 can be combined giving

$$\begin{aligned} \boldsymbol{\beta} &= \epsilon \boldsymbol{\lambda} \delta \mathbf{c} + \mathbf{\Lambda} \cdot \delta \mathbf{c} \\ &= \mathbf{\Lambda}' \cdot \delta \mathbf{c} \end{aligned} \tag{H.27}$$

where the vector $\boldsymbol{\lambda}$ is the vector of diagonal elements of $\boldsymbol{\Lambda}$, Λ_{kk} so the matrix $\boldsymbol{\Lambda}'$ is

$$\Lambda'_{kl} = \begin{cases} \Lambda_{kk}(1+\epsilon) & l = k \\ \Lambda_{kl} & l \neq k \end{cases} \tag{H.28}$$

The method used in this work follows the prescription of Numerical Recipes [125].

1. From an initial guess to the vector $\mathbf{c}$, calculate $\chi^2(\mathbf{c})$.

2. Set ϵ to 0.001.

3. Solve the set of linear equations H.27 for the vector $\delta\mathbf{c}$. Evaluate $\chi^2(\mathbf{c}+\delta\mathbf{c})$.

   - If $\chi^2(\mathbf{c}+\delta\mathbf{c}) \geq \chi^2(\mathbf{c})$ increase ϵ by a factor of 10 and go back to 3.
   - If $\chi^2(\mathbf{c}+\delta\mathbf{c}) < \chi^2(\mathbf{c})$ decrease ϵ by a factor of 10. Update $\mathbf{c} \leftarrow \mathbf{c}+\delta\mathbf{c}$, go back to 3

The iterative cycle was stopped when the fractional decrease in χ^2,

$$\frac{\chi^2(\mathbf{c}) - \chi^2(\mathbf{c}+\delta\mathbf{c})}{\chi^2(\mathbf{c})} \tag{H.29}$$

was less than 0.001.

Appendix I

Matrix elements of the free particle Green's function

The most general expression for the Gaussian matrix elements of the free particle Green's function,

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^+ \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle \tag{I.1}$$

where the functions $\mu_{lmn}^{\alpha,\mathbf{A}}$ and $\mu_{l'm'n'}^{\beta,\mathbf{B}}$ are Cartesian Gaussian functions, with exponent α, β, centered at $\mathbf{A}$ and $\mathbf{B}$ respectively,

$$\mu_{lmn}^{\alpha,\mathbf{A}} = N_{lmn}(r_x - A_x)^l (r_y - A_y)^m (r_z - A_z)^n e^{-\alpha(\mathbf{r}-\mathbf{A})^2}. \tag{I.2}$$

The free particle Green's function G_0^+ in it's spectral representation is (see appendix B)

$$G_0^+ = \lim_{\eta \to 0^+} \frac{1}{(2\pi)^3} \int \frac{e^{i\mathbf{k}\cdot(\mathbf{r_1}-\mathbf{r_2})}}{k^2 - k_0^2 + i\eta} d^3k. \tag{I.3}$$

Substituting this expression into the original matrix element, I.1 gives

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^+ \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle = \lim_{\epsilon \to 0^+} \frac{1}{(2\pi)^3} \int d^3k \frac{\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k} \rangle \langle \mathbf{k} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle}{(k^2 - k_0^2 - i\epsilon)}. \tag{I.4}$$

Utilizing the Cauchy principle value theorem, the integral can be broken into it's principle value integral and a residue term,

$$\begin{aligned}\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^+ \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle &= \frac{1}{(2\pi)^3}\left[\int d^3k \frac{\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k}\rangle\langle \mathbf{k} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}}\rangle}{k^2-k_0^2}\right. \\ &\left. -i\pi\left(\frac{k_0}{2}\right)\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k_0}\rangle\langle \mathbf{k_0} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}}\rangle\right], \end{aligned} \tag{I.5}$$

thus the corresponding matrix element of the principle-value Green's function is given by

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^P \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle = \frac{1}{(2\pi)^3}\int d^3k \frac{\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k}\rangle\langle \mathbf{k} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}}\rangle}{k^2-k_0^2}. \tag{I.6}$$

Substituting the explicit expressions for the Fourier transforms of the Gaussian functions leads to

$$\begin{aligned}&\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^P \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle \\ &= \frac{1}{2^3}N_{lmn}N_{l'm'n'}\left(\frac{1}{\alpha\beta}\right)^{3/2}\frac{i^{l-l'+m-m'+n-n'}}{2^{l-l'+m-m'+n-n'}\alpha^{(l+m+n)/2}\beta^{(l'+m'+n')/2}} \\ &\int d^3k \frac{e^{k^2/4\alpha+k^2/4\beta}e^{i\mathbf{k}\cdot\mathbf{R}}}{k^2-k_0^2}H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right)H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) \\ &H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right)H_{l'}\left(\frac{k_x}{2\sqrt{\beta}}\right)H_{m'}\left(\frac{k_y}{2\sqrt{\beta}}\right)H_{n'}\left(\frac{k_z}{2\sqrt{\beta}}\right)\end{aligned} \tag{I.7}$$

where

$$\mathbf{R} = \mathbf{A} - \mathbf{B}. \tag{I.8}$$

Using the expansion of the plane wave

$$e^{i\mathbf{k}\cdot\mathbf{R}} = 4\pi\sum_{LM} i^L j_L(kR)Y_{LM}(\hat{R})Y_{LM}^*(\hat{k}) \tag{I.9}$$

the matrix element reduces to

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^P \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle = C(lmn;l'm'n') \sum_{LM} i^L f_{LM}(k_0,\alpha,\beta;lmn,l'm'n') \tag{I.10}$$

where

$$\begin{aligned} & C(lmn;l'm'n') \\ &= \frac{1}{2^3} N_{lmn} N_{l'm'n'} \left(\frac{1}{\alpha\beta}\right)^{3/2} \frac{i^{l-l'+m-m'+n-n'}}{2^{l-l'+m-m'+n-n'} \alpha^{(l+m+n)/2} \beta^{(l'+m'+n')/2}} \end{aligned} \tag{I.11}$$

and

$$\begin{aligned} f_{LM} &= \int_0^\infty dk \frac{k^2 e^{-ak^2} j_L(kR)}{k^2 - k_0^2} \int d\hat{k} Y_{LM}^*(\hat{k}) H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right) \\ & H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right) H_{l'}\left(\frac{k_x}{2\sqrt{\beta}}\right) \\ & H_{m'}\left(\frac{k_y}{2\sqrt{\beta}}\right) H_{n'}\left(\frac{k_z}{2\sqrt{\beta}}\right) \end{aligned} \tag{I.12}$$

$$a = \frac{1}{4\alpha} + \frac{1}{4\beta} = \frac{\alpha+\beta}{4\alpha\beta}. \tag{I.13}$$

The angular integrals can be performed by elementary means, leaving a radial integral of the form

$$I_L^P = \int_0^\infty dk \frac{k^P e^{-ak^2} j_L(kR)}{k^2 - k_0^2}. \tag{I.14}$$

The simplest case, $L = 0$ and $P = 2$ is thus

$$\begin{aligned} I_0^2 &= \int_0^\infty dk \frac{k^2 e^{-ak^2} j_0(kR)}{k^2 - k_0^2} \\ &= \frac{1}{R} \int_0^\infty dk \frac{k e^{-ak^2} \sin(kR)}{k^2 - k_0^2} \end{aligned} \tag{I.15}$$

and from tables of Fourier sin transforms [124],

$$\frac{1}{R}\int_0^\infty dk \frac{ke^{-ak^2}}{k^2-k_0^2}\sin(kR) = \frac{\pi}{4R}e^{-ak_0^2}\left[e^{-ik_0R}\mathrm{erfc}\left(i\sqrt{a}k_0 - \frac{R}{2\sqrt{a}}\right)\right.$$
$$\left. -e^{ik_0R}\mathrm{erfc}\left(i\sqrt{a}k_0 + \frac{R}{2\sqrt{a}}\right)\right]. \tag{I.16}$$

Utilizing the properties of the error function, eqn I.16 becomes

$$I_0^2 = \frac{\pi}{2R}e^{-ak_0^2}\mathrm{Re}\left[e^{ik_0R}\mathrm{erf}\left(\frac{R}{2\sqrt{a}} + i\sqrt{a}k_0\right)\right]. \tag{I.17}$$

Integrals with higher values of P and L can be obtained via successive differentiations of this expression with respect to a and R.

For example considering the differential of I_0^2 with respect to R,

$$\begin{aligned}\frac{\partial}{\partial R}I_0^2 &= \frac{\partial}{\partial R}\int_0^\infty dk \frac{k^2e^{-ak^2}j_0(kR)}{k^2-k_0^2} \\ &= -\int_0^\infty dk \frac{k^3e^{-ak^2}j_1(kR)}{k^2-k_0^2} \\ &= -I_1^3\end{aligned} \tag{I.18}$$

which uses the relationship [4]

$$\left(\frac{1}{z}\frac{\partial}{\partial z}\right)^m \left[z^{-n}j_n(z)\right] = (-1)^m z^{-n-m}j_{n+m}(z) \tag{I.19}$$

The differential of I_0^2 with respect to a is,

$$\begin{aligned}\frac{\partial}{\partial a}I_0^2 &= \frac{\partial}{\partial a}\left[\int_0^\infty dk \frac{k^2e^{-ak^2}j_0(kR)}{k^2-k_0^2}\right] \\ &= -\int_0^\infty dk \frac{k^4e^{-ak^2}j_0(kR)}{k^2-k_0^2} \\ &= -I_0^4.\end{aligned} \tag{I.20}$$

Considering the recursion properties of the spherical Bessel functions

$$\frac{(2L+1)}{kR} j_L(kR) = j_{L-1}(kR) + j_{L+1}(kR) \tag{I.21}$$

so that

$$I_L^p = \frac{R}{(2L+1)} \left[I_{L-1}^{p+1} + I_{L+1}^{p+1} \right], \tag{I.22}$$

thus only a certain number of explicit expressions must be derived by successive differentiation, the rest using the recursion relation I.22.

Appendix J

Bound-Free Matrix Elements of the Static Exchange Interaction Potential

The two integrals required for the evaluation of the bound-free matrix elements of the interaction potential are the one electron term,

$$I_1 = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{r} g_i(\mathbf{r}) \tag{J.1}$$

and the two electron term

$$I_2 = \int d\mathbf{r_1} \int d\mathbf{r_2} e^{i\mathbf{k}\cdot\mathbf{r_1}} g_i(\mathbf{r_1}) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} g_j(\mathbf{r_2}) g_k(\mathbf{r_2}) \tag{J.2}$$

where the Gaussian functions g_i, g_j and g_k are of s, p_z or d_{z^2} symmetry and centered at the origin. Expressions for these integrals, for general Cartesian Gaussian functions have been given by McKoy and Watson [23], the specific cases required in section 6.3.1 are given below.

J.1 One Electron Integrals

The general expression for these integrals is given in equation (A16) of [23]. Starting with an s Gaussian function, the integral is

$$
\begin{aligned}
I_{1(s)} &= \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{r} e^{-\alpha r^2} \\
&= \frac{2\sqrt{\pi}}{\alpha} e^{-k^2/4\alpha} I_0^2(1/4\alpha, ik/2\alpha)
\end{aligned} \tag{J.3}
$$

where the integral $I_0^2(a, C)$ is [124]

$$
\begin{aligned}
I_0^2(a, C) &= \int_0^\infty dX\, e^{-aX^2} j_0(CX) \\
&= -\frac{i\pi\alpha}{k} \mathrm{erf}\left(\frac{ik}{2\sqrt{\alpha}}\right).
\end{aligned} \tag{J.4}
$$

Gautschi [126] has published an algorithm for calculating the complex error function.

The p_z and d_{z^2} functions require integrals written $I_L^P(a, C)$ which are related to the $I_0^2(a, C)$ integral,

$$
I_L^P(a, C) = \int_0^\infty dX\, X^{P-2} e^{-aX^2} j_L(CX). \tag{J.5}
$$

These may be found by differentiation of the I_0^2 result with respect to a or C and through the recursion properties of the spherical Bessel functions [96] (see appendix I).

The p_z and d_{z^2} results are [23],

$$
I_{1(p_z)} = -ik_z \frac{\sqrt{\pi}}{\alpha^{5/2}} e^{-ak^2} \left(I_0^2(a, C) + \frac{k I_1^3(a, C)}{2\alpha} \right) \tag{J.6}
$$

$$
\begin{aligned}
I_{1(d_{z^2})} &= -\frac{\sqrt{\pi}}{2\alpha^{5/2}} e^{-ak^2} \left(\frac{I_0^4(a, C)}{3\alpha} - 2I_0^2(a, C) + \frac{I_2^4(a, C)}{3\alpha} \right) \\
&= -k_z^2 \frac{\sqrt{\pi}}{2\alpha^{5/2}} e^{-ak^2} \left(\frac{I_0^4(a, C)}{\alpha} - \frac{k I_1^3(a, C)}{\alpha^2} + \frac{k^2 I_2^4(a, C)}{4\alpha^3} \right),
\end{aligned} \tag{J.7}
$$

where $a = 1/4\alpha$ and $C = ik/2\alpha$.

J.2 Two Electron Integrals

The solution of the integrals from eqn J.2 are given in equation (A12) of [23]. For all s Gaussian functions, written $(s-ss)$ the expression is

$$\begin{aligned} I_{2(s-ss)} &= \int d\mathbf{r_1} \int d\mathbf{r_2} e^{i\mathbf{k}\cdot\mathbf{r_1}} e^{-\alpha r_1^2} \frac{1}{|\mathbf{r_1}-\mathbf{r_2}|} e^{-\beta r_2^2} e^{-\gamma r_2^2} \\ &= \frac{2\pi^2}{(\alpha\delta)^{3/2}} e^{-ak^2} I_0^2(a,C) \end{aligned} \tag{J.8}$$

$a = (\alpha+\delta)/4\alpha\delta$ and $C = ik/2\alpha$, $(\delta = \beta+\gamma)$. The integrals $I_{2(p_z-ss)}$ and $I_{2(d_{z^2}-ss)}$ are simply related to the one electron integrals and can be immediately written

$$I_{2(p_z-ss)} = -ik_z \frac{\pi^2}{\alpha^{5/2}\delta^{3/2}} e^{-ak^2} \left(I_0^2(a,C) + \frac{k I_1^3(a,C)}{2\alpha} \right) \tag{J.9}$$

$$\begin{aligned} I_{2(d_{z^2}-ss)} &= -\frac{\pi^2}{2\alpha^{5/2}\delta^{3/2}} e^{-ak^2} \left(\frac{I_0^4(a,C)}{3\alpha} - 2I_0^2(a,C) + \frac{I_2^4(a,C)}{3\alpha} \right) \\ &= -k_z^2 \frac{\pi^2}{2\alpha^{5/2}\delta^{3/2}} e^{-ak^2} \left(\frac{I_0^4(a,C)}{\alpha} - \frac{k I_1^3(a,C)}{\alpha^2} + \frac{k^2 I_2^4(a,C)}{4\alpha^3} \right), \end{aligned} \tag{J.10}$$

where $a = (\alpha+\delta)/4\alpha\delta$ and $C = ik/2\alpha$.

The final two integrals $I_{2(s-p_z s)}$ and $I_{2(s-d_{z^2} s)}$ arise due to the exchange part of the static exchange potential and are again determined from the expressions of McKoy *et al.*

$$I_{2(s-p_z s)} = ik_z \frac{k\pi^2}{2(\alpha\delta)^{5/2}} e^{-ak^2} I_1^3(a,C) \tag{J.11}$$

$$\begin{aligned} I_{2(s-d_{z^2} s)} &= -\frac{\pi^2}{2\alpha^{3/2}\delta^{5/2}} e^{-ak^2} \left(\frac{I_0^4(a,C)}{2\delta} - 2I_0^2 + \frac{I_2^4}{3\delta} \right) \\ &\quad -k_z^2 \frac{\pi^2}{2\alpha^{3/2}\delta^{5/2}} e^{-ak^2} \frac{k^2 I_2^4}{(2\alpha)^2\delta}. \end{aligned} \tag{J.12}$$

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